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Special number in memory of the Late Prof. R. Srinivasan

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Professor R. Srinivasan was born on 21 April 1938 in Madurai. His father, Dr S. Ramanujam was a distinguished agricultural scientist and a Fellow of the Academy. After a brilliant academic career, Prof. Srinivasan obtained his further training in UK and then returned to India to join the faculty of the Indian Institute of Science in the Physics Department. He reached the rank of full Professor in a relatively short period.

Prof. Srinivasan was one of the leading experts in magnetic resonance, and made significant contributions in the field of ESR spectroscopy of crystals. He also carried out innovative studies on the effect of pressure on magnetic and other properties of crystals. He organised a first rate cryogenic laboratory at the Indian Institute of Science. His originality and creativity were recognised throughout the country and he was awarded the Shanti Swarup Bhatnagar Prize for Physical Sciences in 1982. He was elected a Fellow of the Indian Academy of Sciences in 1979. He passed away on 10 September 1984 when he was barely 46 leaving behind a large number of friends and admirers.

This issue of the Proceedings (Chemical Sciences) is dedicated to the memory of this fine scientist.

C. N. R. Rao
Chairman, Editorial Board
Proceedings (Chemical Sciences)



R. SRINIVASAN (1938 - 1984)

Two-dimensional nuclear Overhauser effect in biomolecules

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Abstract. During the last 5 years, since its first application to biomolecules, two-dimensional nuclear Overhauser effect (2D NOE) has become an extremely powerful technique for assignment of NMR spectra and for elucidation of conformation of biomolecules in solution.

The methodology of the 2D NOE technique, its recent developments and its applications to proteins and oligonucleotides are briefly reviewed.

Keywords. Nuclear Overhauser effect; two-dimensional NMR; peptides and oligonucleotides—structure determination.

1. Introduction

Nuclear Overhauser Effect (NOE), in which non-equilibrium magnetization of spins migrates from one spin to another *via* mutual dipole-dipole relaxation, is a powerful tool for structural elucidation of molecules in liquid state. One-dimensional difference NOE experiments performed by selective saturation or inversion of a resonance have provided a rich source of structural information in biomolecules, but require a large number of selective experiments. Application of two-dimensional (2D) techniques for monitoring NOE in biomolecules had a revolutionary effect in the study of biomolecular structures by NMR.

The scheme for 2D NOE experiments first proposed for chemical exchange by Jeener (1977) and exploited mainly for study of chemical exchange by Meier and Ernst (1979) and Jeener *et al* (1979) is given in figure 1. Non-equilibrium *z*-magnetization of all spins produced by the second 90° pulse after frequency labelling during t_1 , undergoes dipole-dipole relaxation and chemical exchange, if any, during a fixed mixing period τ_m at the end of which the third 90° pulse reads the state of each spin as a function of t_2 . The rate equations governing this transfer during τ_m (Jeener *et al* 1979) are similar to those of 1D transient NOE experiments (Solomon 1955; Kalk and Berendsen 1976).

The first 2D NOE spectrum of a biomolecule (Anil Kumar *et al* 1980a) is shown in figure 2. The numerous cross-peaks produced in this spectrum provide a rich source of information on the proximity of various protons in the biomolecule. Biomolecules which reorient slowly on the NMR time-scale such that $\omega\tau_c \gg 1$ where ω is the resonance frequency and τ_c is the characteristic reorientation time, known as correlation time of the molecule, give negative NOE and favourable cross-peak intensity in the 2D NOE experiment (Macura and Ernst 1980). Small molecules which reorient faster, for which $\omega\tau_c \ll 1$ and give positive NOE, yield poor cross-peak intensity in the 2D NOE experiment. Molecules for which $\omega\tau_c \sim 1$ give no NOE. The effects of *J* coupling on the 2D NOE experiment have been studied (Macura *et al* 1981, 1982). Details of the experimental procedure and parameters required for proton 2D experiments in proteins including details of phase cycling employed have been described (Wider *et al* 1984).

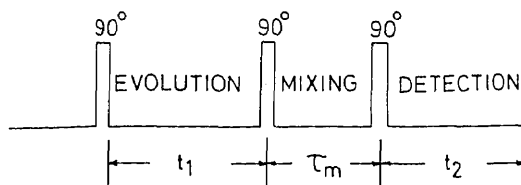


Figure 1. Pulse scheme for 2D NOE experiment. Signal is collected during t_2 , for a complete set of t_1 values and for a fixed interval τ_m during which nuclear Overhauser effect takes place. The phase cycling for cancellation of axial peaks and transverse magnetization after the second pulse and for quadrature detection in both dimensions has been described (Wider *et al* 1984).

2. Methodology of 2D NOE

The build-up rate of 2D NOE has been studied as a function of mixing time τ_m (Anil Kumar *et al* 1981). In biomolecules the spin-diffusion tends to make the NOE information non-specific and experiments with controlled mixing time have been suggested to overcome this problem in 1D NOE schemes (Krishna *et al* 1978; Gordon and Wuthrich 1978; Dubs *et al* 1979). Furthermore, theoretically it has been shown that the initial build-up rate of 2D NOE is directly proportional to r^{-6} , where r is the distance to the nearest proton from the proton of interest (Macura and Ernst 1980). While factors such as differences in linewidths, relaxation times, multiplicity of coupling partners and effects of filter functions make it difficult to use the 2D NOE information quantitatively, attempts are underway to utilize the 2D NOE data for quantitative distance measurements (Wagner *et al* 1984; Keepers and James 1984; James 1984). So far, however, distance information from 2D NOE has been effectively utilized in qualitative or at best in semi-quantitative manner as upper and lower bounds on distances.

Another important feature of 2D NOE and 2D correlated (cosy)* experiments is the ability to perform these experiments in H_2O solutions and obtain information on exchangeable protons (Anil Kumar *et al* 1980b; Wider *et al* 1983). This has been a key development in obtaining complete assignments and structural information on biomolecules. For suppression of H_2O signal in 2D NOE experiment three schemes have been suggested. The most widely used scheme utilizes selective saturation of H_2O resonance by irradiation (Anil Kumar *et al* 1980b; Wider *et al* 1983). Cutnell (1982) suggested replacement of last 90° pulse by 2-1-4 sequence (Redfield *et al* 1975) with a null at H_2O resonance position in its excitation profile. Another technique utilizes the observation that the T_1 of H_2O protons is much longer than those of protein resonances. A non-selective inversion by a 180° pulse followed by a recovery period $= \tau_{null}$ for H_2O resonance, precedes the 2D NOE experiment, accomplishing effective suppression of H_2O signal, almost full recovery of protein signals and unmasking of protein resonances buried under the H_2O signal (Basus 1984).

2D NOE experiment is utilized in an interactive manner with cosy for spectral

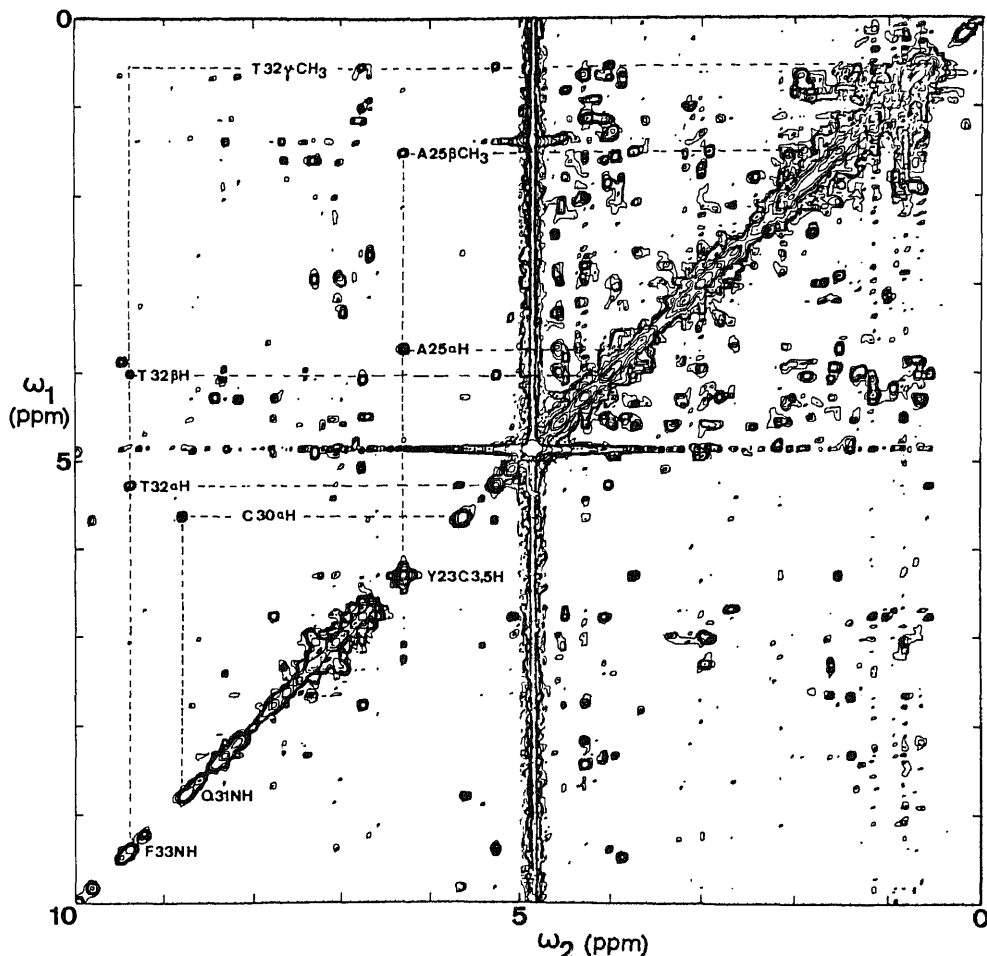


Figure 2. 2D NOE spectrum of basic pancreatic trypsin inhibitor (BPTI) recorded at 360 MHz and $\tau_m = 100$ m sec. The protein concentration was 20 mM in D_2O , at pH = 3.8 and $T = 18^\circ C$. The spectral width = 4000 Hz and 512 data points were collected in each dimension, with total data accumulation time of 18 hr. Shifted sine bell filtering has been utilized in both dimensions and an absolute intensity contour plot is shown here. Some of the β -sheet NOE's; those between phenylalanine NH proton (F33NH) and threonine (T) C^α , C^β and C^γ protons, between glutamine (Q) NH proton and cysteine (C) C^α proton and between tyrosine (Y) ring protons and alanine (A) C^α and C^β protons are indicated by broken lines. Subsequent analysis of this data (Wagner *et al* 1981), and additional data (Wagner and Wüthrich 1982) have yielded essentially complete assignment of all backbone and C^β proton resonances (from Anil Kumar *et al* 1980a).

assignment and sequence determination. Combined with one triangle of cosy data and other triangle of NOE data, diagrams such as cosy-NOESY have yielded features which are used for tracking down secondary structures such as β -sheet in biomolecules (Wagner

from a known NH proton resonance, NOE gives strong cross-peak to preceding C^αH proton, which in turn has cross-peak with NH proton of the same residue in the cosy. Continuing from the NH proton the resonance assignments of the backbone resonances of the entire β -secondary structure can be obtained (Wagner *et al* 1981).

3. Applications to proteins

The information from 2D NOE has been effectively utilized by Wüthrich and coworkers for structure determination of biomolecules. The NOE between NH proton of adjacent aminoacid residues of a polypeptide chain has been called d_2 -connectivity, while those between NH proton and C^αH and C^βH protons of preceding residue respectively as d_1 and d_3 connectivity (Billeter *et al* 1982). Sequential resonance assignments have been obtained in the backbone region of several small proteins, by careful and large scale application of 2D techniques, the strategy for which is summarized in Wüthrich *et al* (1982) and Wüthrich (1983). Essentially complete resonance assignments have been obtained for backbone and C^βH proton resonances of basic pancreatic trypsin inhibitor (BPTI), a globular protein of 56 aminoacid residues (Wagner and Wüthrich 1982a), glucagon bound to perdeuterated micelles (Wider *et al* 1982), trypsin inhibitor E (Arseniev *et al* 1982), proteinase inhibitors IIA and IIB from Bull Seminal Plasma (BUSI IIA and IIB) (Strop *et al* 1983a, b) and cardiotoxin V^{II} (Steinmetz *et al* 1981 and Hosur *et al* 1983).

Distance geometry algorithms have been written with aims of obtaining three-dimensional conformation of small proteins with distance constraints as obtained from 2D NOE data (Braun *et al* 1981; Havel and Wüthrich 1984a, b). The new distance geometry program DISGOE (Havel and Wüthrich 1984) capable of computing complete spatial structures of polypeptide chains upto ca. 100 aminoacid residues, has been tested for its ability to compute structures of biomolecules from 2D NOE data, by comparing the calculated structure of BPTI to its known crystal structure (Havel and Wüthrich 1985). Using the resonance assignments mentioned above, the distance information as obtained from 2D NOE and the distance geometry algorithms, three-dimensional structures have been calculated for glucagon (Braun *et al* 1983), BUSI IIA (Williamson *et al* 1984), BPTI (Wagner *et al* 1984) and portions of micelle-bound melittin (Brown *et al* 1982). The strategies utilized for the above structure determination have been outlined by Wüthrich *et al* (1983, 1984).

Various 2D techniques including 2D NOE have been utilized for studying the solution structure of Alamethicin (Banerjee *et al* 1983) and gramicidin A double helix (Arseniev *et al* 1984a). Arseniev *et al* (1984b) have also studied the three-dimensional solution structure of a short insectotoxin I₃A using various 2D NMR techniques including 2D NOE, have utilized the distance geometry algorithm of Braun *et al* (1981) and found similarity with the known single crystal α -helical and antiparallel β -structure of a homologous 'long' toxin v-3. Wemmer and Kallenbach (1983) studied the 18 aminoacid residue neurotoxin apamin, obtained essentially complete resonance assignments using cosy and 2D NOE, and obtained evidence for secondary structures consisting of a β turn and a α -helix.

Zuiderweg *et al* (1983, 1984a, b) have studied the structure of the headpiece of LAC repressor, residue 1-51, and found that the headpiece contains three α -helices connected

assignments in oligonucleotides along with COSY experiments. Usually these DNA fragments are in some well-defined helical conformation such as B-DNA and a few typical NOEs are able to confirm such a configuration. The remaining NOEs in the molecule are then used for resonance assignment and conformation determination in an interactive manner.

Hare *et al* (1983) studied self-complementary DNA sequence d(CGCGAATTCGCG) by the above 2D techniques, obtained complete resonance assignments and from the observed NOE data concluded that in solution this helix is right-handed close to the B-DNA form in conformity with the crystallographic structure. Scheek *et al* (1984) used this algorithm to obtain resonance assignments in a mixture of two synthetic complementary heptamers d(TGAGCGG) and d(CCGCTCA) forming a duplex. Broido *et al* (1984) used 500 MHz, phase-sensitive 2D NOE experiments performed with several mixing times to obtain complete resonance assignments in self-complementary octamer duplex [d-(GGAATTC)]₂, the largest oligonucleotide yet assigned. Weiss *et al* (1984a,b) carried out assignments of major groove sugar protons of the 17 base pair DNA operator site O_L 1 by 2D NOE and COSY. Haasnoot *et al* (1983) have done sequential assignment and conformational analysis of d(CG) r(CG) d(CG) using COSY and 2D NOE.

Feigon *et al* (1982, 1983) have used 2D NOE along with COSY and 1D experiments for obtaining complete proton resonance assignments in double stranded synthetic DNA decamer d(ATATCGATAT). The observed NOEs further establish that the nucleotides have an anti-conformation of the bases relative to sugar which is consistent with the B-form of DNA. Broido and Kearns (1982), on the other hand, have used 2D NOE and other relaxation measurements to conclude that poly C forms a left-handed helical structure in neutral solution.

Hilbers *et al* (1983) have studied the solution structure of yeast tRNA^{phe} using 2D NOE, have totally assigned imino proton spectrum, and have shown that the principal elements of x-ray structure of tRNA *i.e.* the hydrogen bonding network and the stacking of the stems upon one another, are also found in solution. The imino protons of several pure *E. coli* isoacceptor tRNA species have been assigned by 2D NOE in H₂O solution (Reid *et al* 1984). Borah *et al* (1984) have utilized phase-sensitive 2D NOE spectra, for studying three-dimensional conformation of several sonicated poly-deoxynucleotides in solution. They find that poly(dAdT)·poly(dAdT) and poly(dGm³dc)·poly(dGm³dc) in low salt and poly(dAdT)·poly(dAdT) in high salt are right-handed B-structures, in contrast to suggestions that poly(dAdT)·poly(dAdT) exists as a left-handed form either in low or high salt. Ravikumar *et al* (1984) used 2D methods, including 2D NOE, for studying the solution structure of d(CG)₆ in low salt concentration and found indications of B-DNA structure, at least in some parts of the molecule.

Clore and Gronenborn (1985) have recently reviewed the use of 1D and 2D NOE for three-dimensional structure determination of DNA and RNA oligonucleotides in solution and have studied the solution structure of DNA hexamer d(CGATACG) and octamer d(ACGCGCGT) (Clore and Gronenborn 1984; Clore *et al* 1985).

2D NOE has been utilised for determination of sequence and linkage sites in ceramide trisaccharide (Prestegard *et al* 1982) and for sequence and linkage site determination in

oligosaccharides of gangliosides (Koerner *et al* 1983). Homans *et al* (1984) have used 2D NOE along with other 1D and 2D NMR techniques for structural and conformational analysis of oligosaccharides.

5. Other developments

5.1 Accordion 2D NOE spectroscopy

Bodenhausen and Ernst (1981, 1982) extended the 2D NOE experiment into third time dimension without increasing the experimental time. The mixing time τ_m of 2D NOE scheme, figure 1, was incremented in concert with t_1 , such that $\tau_m = kt_1$ where k is a constant, and appropriately named this scheme as Accordion spectroscopy. The lineshapes of the cross and diagonal peaks of the resulting 2D NOE spectrum contain information on the rate constants governing the growth and decay of these peaks. It was shown that these rate constants could be extracted, in a straightforward manner, by appropriate data handling. However, whenever lines are overlapped or have multiplet structure as happens rather often in proton NMR spectra of biomolecules, the analysis of the data becomes complex. So far, application of Accordion spectroscopy has been limited to study chemical exchange networks *via* carbon-13 experiments where non-overlapping resonances are obtained (Huang *et al* 1981; Bodenhausen and Ernst 1982).

5.2 Combined COSY/NOESY experiments

Recently two groups have independently suggested collection of data following both the second and third pulses in the 2D NOE scheme, thus making it possible to collect both COSY and NOESY data in a single experiment, with the resolution in ω_2 dimension for COSY limited to $1/(2\tau_m)$ (Gurevich *et al* 1984; Haasnoot *et al* 1984). Appropriate phase cycling for carrying out these experiments have been given.

5.3 Relayed coherence transfer 2D NOE

Wagner (1984) has suggested combining a coherent transfer step along with 2D NOE experiment either before the NOE transfer or after, and named it Relayed NOESY. These experiments have been suggested to transfer a NOE peak from crowded to sparse spectral region and to solve ambiguities in the interpretation of NOESY cross-peaks.

5.4 CIDNP and 2D

Scheek *et al* (1984) have combined photochemically-induced dynamic nuclear polarization (photo-CIDNP) and 2D techniques (COSY, NOESY and INEPT) for identifying selectively three aromatic amino acid residues (tryptophan, tyrosine and histidine) on the surfaces of proteins. The 2D techniques are preceded by a saturation pulse and a short laser pulse to generate CIDNP. Interesting 2D spectra which lack the symmetry of

difficult or impossible to obtain from conventional NMR methods. provided large number of distance constraints making it possible dimensional structures of polypeptide chains in aqueous solution, most powerful 2D technique for biological systems.

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Some applications of ^{13}C NMR spectroscopy in heterocyclic structure assignments*

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Abstract. The usefulness of ^{13}C NMR spectral data in solving otherwise intractable structural problems in heterocyclic chemistry is illustrated with ring systems such as imidazoles, pyrazoles, thiazoles, pyrimidines, benzodioxoles, benzodioxanes, benzoxazines, benzothiazines, quinoxalines, imidazopyrazoles, imidazothiazoles, pyridobenzoxazines, thiazolo-benzimidazoles, thiazinobenzimidazoles, pyrimidobenzimidazoles, naphthodioxanes and perimidines. For example, using both chemical shifts and coupling constants, especially the one across three bonds, it has been possible to assign unique structures to the addition products of acetylenedicarboxylic esters to a variety of dinucleophiles such as thioureas, guanidines, 2-aminophenol, 2-aminothiophenol, 1,8-dihydroxy and 1,8-diaminonaphthalenes and 8-hydroxy-1,2,3,4-tetrahydroquinoline. These parameters also allow easy differentiation of isomeric imidazoles arising from N-alkylation of nitroimidazoles or nitration of imidazoles and of isomeric pyrazoles obtained from the reaction of hydrazines with ethoxymethylene derivatives of 1,3-dicarbonyl compounds.

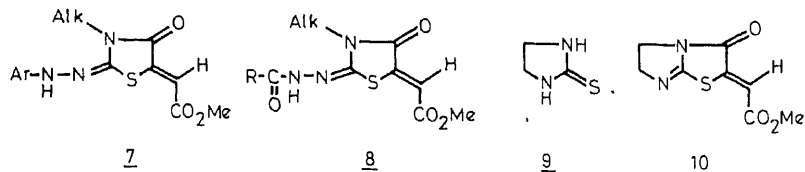
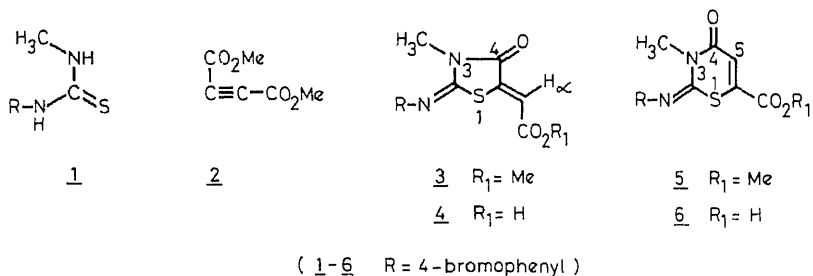
Keywords. ^{13}C chemical shifts; C-H coupling constants.

1. Introduction

NMR spectroscopy has developed into a versatile and powerful tool for structural assignments in organic chemistry. Until about a decade ago, NMR information was confined mostly to the protons at the periphery of organic molecules and did not extend widely to carbon atoms which form the basic core. This was due to the fact that ^{12}C , although present in great abundance has no nuclear spin and hence does not give a NMR signal. On the other hand ^{13}C has a spin of $1/2$ and does generate a signal. However, due to its extremely low natural abundance aggravated by an unfavourable gyromagnetic ratio, the nucleus is bedevilled by very poor sensitivity. Hence routine measurements of ^{13}C NMR spectra in natural abundance were not feasible earlier. The disability has disappeared with the advent of pulsed excitation combined with Fourier transform techniques which are now featured in commercial FT NMR spectrometers. The ready availability of ^{13}C NMR spectra has offered the organic chemists a weapon *par excellence* for diverse investigations including structural assignments in all their intimate details (Nagarajan 1980; Wehrli and Wirthlin 1976). In recent years we have used the technique efficiently in elucidating structures of a variety of heterocycles arising from reactions such as addition of acetylene dicarboxylic esters to dinucleophiles and condensation of hydrazines with ethoxymethylene derivatives of 1,3-dicarbonyl compounds as well as of products of alkylation and acylation of azoles. We wish to review briefly our

2.1 Products from thiocarbamoyl derivatives

The reaction proceeds with great facility and often gives rise to unique products whose structures have been the subject of controversy, with thiazolinones (type 3) (Hendrikson *et al* 1964; Nagase 1973) and thiazinones (type 5) (Lown and Ma 1967) being the major contenders. With unsymmetrical thioureas, either of the two nitrogen atoms can participate in the formation of the lactam. Finally in the case of thiazolinones, the carboalkoxymethylidene unit can be part of a fumarate (Z configuration) or a maleate (E configuration) skeleton. We were able to marshal the help of ^{13}C NMR spectra especially $^3J_{\text{CH}}$ coupling for establishing the thiazolinone structures uniquely (Vögeli *et al* 1978). For example the ^{13}C NMR spectrum of the product from N-(4-bromophenyl)-N¹-methyl-thiourea (1) and dimethyl acetylene dicarboxylate (2) (DMAD) showed the signal due to the lactam carbon atom at 164.4 ppm which was involved in two $^3J_{\text{CH}}$ interactions—one with a *cis*-placed proton to the extent of 5.3 Hz and another with the adjacent N-methyl protons to the tune of 2.6 Hz. This allowed us to deduce the structure of the product uniquely as 3, ruling out 5. Alkaline hydrolysis of 3 followed by acidification afforded a separable mixture of the thiazolinone carboxylic acid 4 and the thiazinone carboxylic acid 6 which were readily distinguished by their ^{13}C NMR spectra (Nagarajan *et al* 1983). The relevant data are: 4 $\delta\text{C}(4)$ 165.0 ppm; $^3J_{\text{C}(4)\text{H}(\alpha)}$ 6, $^3J_{\text{C}(4)\text{H}(\text{CH}_3)}$ 2.8 Hz; for 6: $\delta\text{C}(4)$ 162.5 ppm; $^2J_{\text{C}(4)\text{H}(5)}$ 2.5 and $^3J_{\text{C}(4)\text{H}(\text{CH}_3)}$ 1.5 Hz. Structural assignments of 4 and 6 were substantiated by x-ray crystallographic studies.

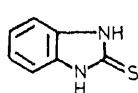


Carboxymethylidenethiazolinone structures were similarly rigorously assigned to the products from various substituted monoalkyl, monoaryl, dialkyl, alkyl aryl, diaryl, aryl arylalkyl and diarylalkyl-thioureas as well as to those from cyclic thioureas, piperidine-1-thiocarboxamide and thiobenzamide (Vögeli *et al* 1978). With aryl alkyl (*e.g.* N-methyl-N'-phenyl) and aryl arylalkyl (*e.g.* N-benzyl-N'-phenyl) thioureas, regioselective, often regiospecific reaction occurred to afford products in which the more basic alkyl or aralkyl substituted N atom was involved in the lactam bond. Steric

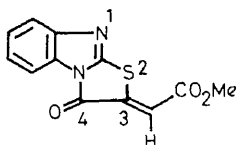
diphenyl)-N'-methylthiourea and N-phenyl-N'-(t-butyl) thiourea gave 2-(2-diphenyl) and 2-(t-butyl)imino-3-phenylthiazolinones as the major isolable products. Both were hydrolysed by concentrated HCl to the same 5-carboxymethylidene-3-phenylthiazoline-2,4-dione as the one obtained from acid hydrolysis of the DMAD adduct of N,N'-diphenyl thiourea. N-Ethyl-N'-methylthiourea afforded both possible products with the 2-ethylimino ($\text{R} = \text{Et}$) predominating over the 2-methylimino derivative in the ratio of 3:2, while N-(t-butyl)-N'-methylthiourea gave rise to only $\text{R} = \text{t-Bu}$ (Nagarajan 1978). In all these cases, the signal due to C(4) showed appropriate multiplicity, the last one for example, having only one $^3\text{J}_{\text{CH}}$ coupling with a *cis*-placed vinyl proton. 1-Aryl and 1-acyl 4-alkylthiosemicarbazides afforded **7** and **8** respectively, structure assignments arising from ^{13}C NMR data (Nagarajan 1978).

The reaction of imidazolidinethione (**9**) produced the imidazothiazoline **10** uniquely. On the other hand benzimidazoline-2-thione (**11**) was reported to afford a mixture of two products in varying proportions, depending upon methanol or acetic acid being the solvent (Mckillop *et al* 1978). The product that could be obtained pure readily was considered to be **12** and the other one suspected to be **13**. We were successful in isolating pure **13** and in using ^{13}C together with ^1H NMR data for definitive total structure assignments (Nagarajan *et al* 1979): **12** $\delta\text{C}(4)$ 157.4; $^3\text{J}_{\text{CH}}$ 6 Hz; **13** $\delta\text{C}(5)$ 159.1; $^2\text{J}_{\text{CH}} \leq 1$ Hz. **12** and **13** could be equilibrated in methanol under acid catalysis with **13** preponderating in the mixture, while methanolic sodium methoxide transformed **12** completely into **13** (Wade 1979). The reaction course of DMAD with **11** is different from the one with **9** perhaps because of the strain involved in fusing a second 5-membered ring to benzimidazole, which renders **13** stabler in relation to **12**. A similar behavioural dichotomy was observed with acyclic guanidines and 2-aminobenzazoles (*vide infra*).

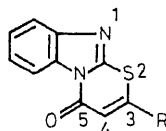
Ethyl phenyl propiolate and **11** on the other hand gave thiazinone **14** as the only isolable product. NMR spectral data were used to revise an earlier incorrect structure assignment (Nair *et al* 1979a).



11

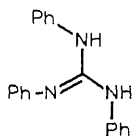


12

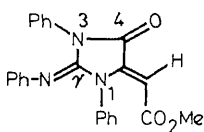


13 R = CO₂Me

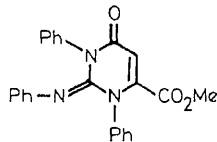
14 R = Ph



15



16



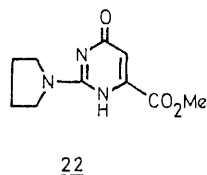
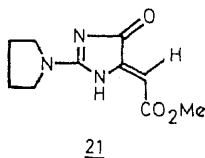
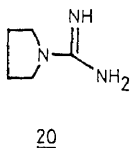
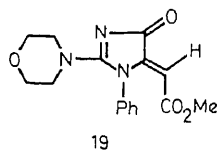
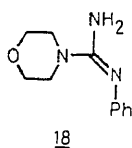
17

2.2 Products from guanidines

N,N',N''-triphenylguanidine (**15**) and DMAD have been reported to yield a pyrimidinone **17** (Lown and Ma 1967). ^{13}C NMR spectral data revealed beyond doubt that the product

observation in the ^1H NMR spectrum of 16 was the heavy shielding of the methoxyl protons by N-phenyl group: $\delta(\text{O})\text{CH}_3$ 3.15 ppm. Structure 16 has been confirmed by x-ray studies (Acheson and Wallis 1981). Similar observations with the product of guanidine 18 led us to assign structure 19 to the product (Nagarajan 1978; Nagarajan *et al* 1985a).

Pyrrolidine-1-carboxamidine 20 and DMAD led to the formation of imidazolidinone 21 isolated as its salt with 20. Incidentally 21 happened to be identical with a preparation obtained from treatment of the product from thiourea and DMAD with pyrrolidine followed by cyclisation with acetic anhydride and thus structure 22 assigned to the last compound (Winterfeldt and Nelke 1967) needs to be revised (Nagarajan *et al* 1985a).

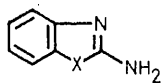


2.3 Products from 2-aminobenzimidazole 23 and 2-aminobenzothiazole 24 and DMAD

Unlike acyclic guanidines, the product from 23 was a pyrimidobenzimidazole 25 as evident from the multiplicity of the signals due to the ester $\text{C}=\text{O}$ carbon atom (δ 161.1 ppm; dxq; $^3J_{\text{CH}(2)}$ 4.3, $^3J_{\text{CH}(\text{OCH}_3)}$ 3.9 Hz); lactam carbon atom (δ 165.3 ppm; s). The product 26 from 2-aminobenzothiazole (24) exhibited similar features in the ^{13}C NMR spectrum. These data would have fitted both structures 25 (26) and 27. However in their ^1H NMR spectra, a signal due to a highly deshielded aromatic proton (H^*) was not observed, thus ruling out 27 in favour of 25 (26) (Vögeli *et al* 1978). These structures had derived support earlier from x-ray studies.

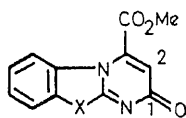
2.4 Products from catechol, 2-aminophenol, 8-hydroxy-1,2,3,4-tetrahydroquinoline, o-phenylenediamine and 2-aminothiophenol

Addition of catechol to DMAD in the presence of a little sodium methoxide afforded in high yield a 1 : 1 adduct. This was formulated as the benzodioxole derivative 28 and not the dioxane 30. Structure 28 followed from a study of ^1H and ^{13}C NMR spectra. Diagnostic ^{13}C data were signals at about δ 43 (t, $^1J_{\text{CH}}$ 130 Hz) and 98 ppm (t, $^2J_{\text{CH}}$ 6 Hz) in addition to the observation of two sets of signals for the ester CH_3 and $\text{C}=\text{O}$ carbon atoms. Alkaline hydrolysis of 28 and acidification gave a mixture of acids 29 and 31 which afforded the methyl ester 32. The lactone carbon atom in 32 gave a NMR signal at



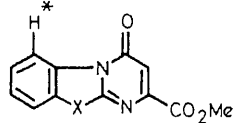
23 X = NH

24 X = S

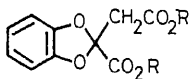


25 X = NH

26 X = S

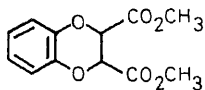


27 X = NH, S

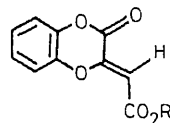


28 R = CH₃

29 R = H



30

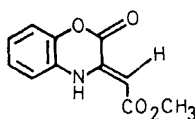


31 R = H

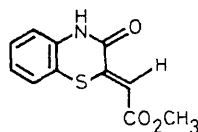
32 R = CH₃

153.8 ppm as a doublet with $^3J_{\text{CH}}$ 3.7 Hz and the ester C=O carbon atom at 163.3 ppm split into a quartet (Vögeli *et al* 1978). In contrast to catechol, 2-aminophenol and 2-aminothiophenol upon reaction with DMAD yielded products with the loss of elements of methanol. A detailed analysis (Vögeli *et al* 1978) of their ^{13}C NMR spectra confirmed structures 33 and 34 respectively assigned earlier from other considerations.

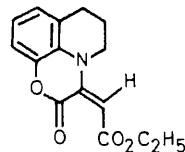
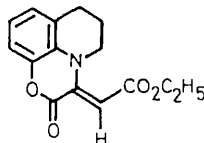
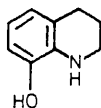
The reaction of 8-hydroxy-1,2,3,4-tetrahydroquinoline (35) with acetylenedicarboxylic esters can give rise to six possible products. Interestingly the singular homogeneous (TLC) product that was obtained using the diethyl ester turned out to be an equilibrating mixture of 36 and 37 (Vögeli *et al* 1978; Nair *et al* 1979b). The two geometrical isomers differ in the coupling constants of the ring C=O carbon atom with the vinyl proton (5.3 and 11.3 Hz respectively). This represents a unique example in our comprehensive studies wherein both E and Z isomers were encountered and identified by the greater magnitude of the *trans* $^3J_{\text{CH}}$ coupling constant compared to that of *cis* $^3J_{\text{CH}}$ (Vögeli and Philipsborn 1975).



33

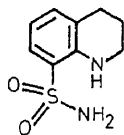
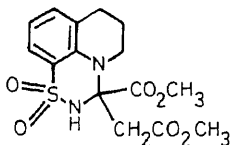
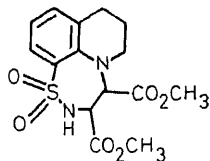
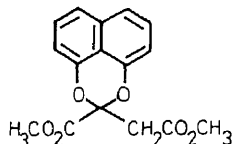
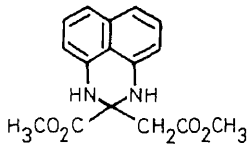
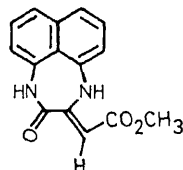


34



2.5 Product from 1,2,3,4-tetrahydroquinoline-8-sulphonamide (38)

Reaction of 38 with DMAD gave a single 1 : 1 adduct for which structures 39 and 40 were possible. 39 was the obvious choice on the basis of ^{13}C NMR data $\delta\text{C}(\underline{\text{CH}_2\text{COMe}})$ 39.5 ppm; t, $^1\text{J}_{\text{CH}}$ 135 Hz; $\delta\text{C}(\text{C}=\text{N})$ 77.8 ppm; t, $^2\text{J}_{\text{CH}}$ 5 Hz (Nagarajan *et al* 1985b).

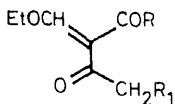
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2.6 Products from the reaction of DMAD with 1,8-dihydroxynaphthalene and 1,8-diaminonaphthalene

The behaviour of 1,8-dihydroxynaphthalene towards DMAD paralleled that of catechol and afforded the 1 : 1 adduct 41 in 50% yield; besides ^1H NMR data, ^{13}C data were used to derive the structure; mainly a triplet at 42.7 ($^1\text{J}_{\text{CH}}$ 133 Hz), triplet at 98.1 ($^2\text{J}_{\text{CH}}$ 5.9 Hz), quartets at 52 and 53.0 ($^1\text{J}_{\text{CH}}$ 148 Hz) and overlapping quartets at 167.5 and 166.9 ppm with small coupling constants (Nair *et al* 1979b).

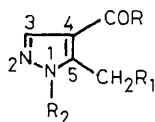
Somewhat in contrast, 1,8-diaminonaphthalene produced a separable mixture of two compounds. One was the perimidine 42 ($\delta\text{C}(\underline{\text{CH}_2})$ 43.6; t, $^1\text{J}_{\text{CH}}$ 137 Hz, $\delta\text{C}(\text{C}=\text{N})$ 69.4; t, $^2\text{J}_{\text{CH}}$ 6 Hz) which had been given an incorrect structure earlier (Iwanami 1962). The second product was identified as 43 (Nair *et al* 1979b).

3. Pyrazoles from monosubstituted hydrazines and ethoxymethylene derivatives of 1,3-dicarbonyl compounds (Nagarajan 1982; Nagarajan 1983, Nagarajan *et al* 1985c).



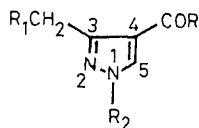
44 R = CH₃, R₁ = H

45 R = CH₃, R₁ = OCH₃



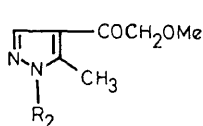
46 R = CH₃, R₁ = H

47 R = CH₃, R₁ = OCH₃

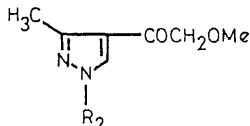


48 R = CH₃, R₁ = H

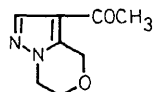
49 R = CH₃, R₁ = OCH₃



50



51



52

The reaction of 44 with monosubstituted hydrazines can give rise to one or both of two products 46 and 48, if we make the reasonable assumption that the incipient formyl group ($=\text{CHOEt}$) in 44 will initiate the reaction with R_2NHNH_2 . The nature and composition of products will then depend upon the relative nucleophilicities of the two hydrazine N atoms which in turn are determined by the nature of R_2 . In the case of ethoxymethylene derivatives of unsymmetrical 1,3-diketones like 45, four possibilities 47, 49, 50 and 51 arise. The determining factors for the composition of the product mixture will be the relative nucleophilicities of the two N atoms in R_2NHNH_2 and the electrophilicities of the two C=O groups, COR and COCH_2R_1 . In the case of 45, the CO group attached to CH_2OMe can be justifiably expected to be stronger and more reactive compared to the one hooked to a CH_3 group.

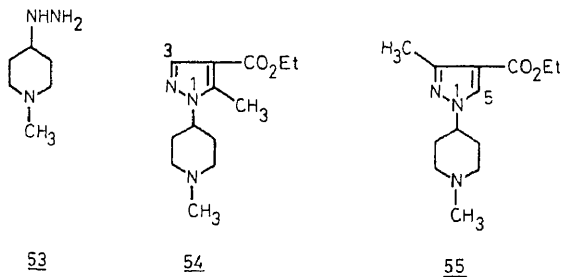
We have used ^{13}C NMR spectroscopy advantageously in reinvestigating the earlier work and expanding its horizons. Thus, the reaction of 44 with 2-hydroxyethyl hydrazine afforded 48 ($\text{R}_2 = \text{CH}_2\text{CH}_2\text{OH}$) as the major and 46 ($\text{R}_2 = \text{CH}_2\text{CH}_2\text{OH}$) as the minor products, correcting the earlier literature where the sole products obtained in high yields using 2-hydroxyethyl and other alkyl hydrazines were considered to be 46 (Arya 1968; Arya *et al* 1971). Critical for the revised assignments were chemical shifts and splitting patterns of the proton-bearing carbon atom in the pyrazole rings: C-3 in 46 ($\text{R}_2 = \text{CH}_2\text{CH}_2\text{OH}$) δ 141.2 ppm, d, $^1\text{J}_{\text{CH}}$ 185 Hz. C-5 in 48 ($\text{R}_2 = \text{CH}_2\text{CH}_2\text{OH}$) δ 135.8 ppm; d x t; $^1\text{J}_{\text{CH}}$ 185, $^3\text{J}_{\text{CH}}$ 2.5 Hz. In fact for all the alkyl or aralkyl hydrazines studied 48 was the major and in a few cases the sole product and 46, the minor one. With aryl hydrazines, on the other hand, consistent with the greater nucleophilicity of the unencumbered N atom, 46 ($\text{R}_2 = \text{Ar}$) was the major product and in the case of 4-nitrophenyl hydrazine, the sole product. As with the pairs 46 ($\text{R}_2 = \text{alkyl}$) and 48 ($\text{R}_2 = \text{alkyl}$), C-3 in 46 ($\text{R}_2 = \text{Ph}$) appeared more downfield (δ 141.9 ppm) than C-5 in 48 ($\text{R}_2 = \text{Ph}$) (δ 130.8 ppm). Although a long-range $^3\text{J}_{\text{CH}}$ coupling was not possible in 48 ($\text{R}_2 = \text{aryl}$) compared to 48 ($\text{R}_2 = \text{methyl}$ etc), the differences in the chemical shifts of the two series was sufficiently pronounced to be of diagnostic utility. The differences are obviously to be attributed to the fact that C(3) in 46 is attached to a biligant N atom while C(5) in 48 is tied to a triligant one. Again in the case of aryl hydrazines and 44, substitution at position 4 with electron-donating substituents increased the nucleo-

As a consequence of these studies, it became clear that unlike in the case of alkyl hydrazines, pyrazoles obtained earlier from aryl hydrazines and **44** were indeed 1-aryl-4-acetyl-5-methyl derivatives **46** and structures assigned to Mannach bases obtained from them then needed no revision (Arya 1966; Arya *et al* 1969).

2-Hydroxyethyl hydrazine and **45** afforded a mixture of the two pyrazoles **47** and **49** ($R_2 = CH_2CH_2OH$) the former being the minor product. **50** and **51**, if formed, were in undetectable quantities. Crucial ^{13}C NMR data were as follows: **47**: C-3, δ 141.2 ppm; d, $^1J_{CH}$ 186 Hz; **49** C-5, δ 135.8 ppm; d x t; $^1J_{CH}$ 189, $^3J_{CH}$ 2.4 Hz. Use of these data for structure assignments was convincingly vindicated when **47** underwent HBr mediated dimethylative ring closure to **52**.

Solvent-induced proton shifts (Takeuchi *et al* 1978; Nagarajan *et al* 1982a) could be used to distinguish between **46** and **48** with limited validity; but ^{15}N NMR spectroscopy provided clear-cut answers: N(2) in **46** showed a large geminal coupling with H(3) to the extent of about 13 Hz which was not possible with **48** (Chen *et al* 1983).

Pyrazole formation from ethoxymethylene derivatives of other unsymmetrical 1,3-dicarbonyl compounds like benzoyl acetone, acetoacetonitrile and ethyl acetoacetate was also studied using ^{13}C NMR spectroscopy. Earlier patterns were maintained in these cases as well, except that in the reaction of the last compound with 1-methyl-4-piperidylhydrazine (**53**), a mixture of **54** ($\delta C(3)$ 140.6, d) and **55** ($\delta C(5)$ 131.0; d x d) was formed in the ratio of 5:2 revealing a role for steric factors.



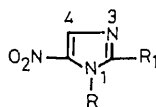
4. Alkyl and aryl derivatives of nitroimidazoles and nitropyrazoles

5-Nitroimidazole derivatives with potent antimicrobial properties (Nair and Nagarajan 1983; Nagarajan *et al* 1984) are obtained by nitrating 1-substituted imidazoles or by alkylation/arylation of 1-unsubstituted-4-nitroimidazoles. These are accompanied in these reactions by 4-nitro isomers which are spectacularly inactive *in vivo*. Among the spectroscopic techniques available to differentiate between the two series, solvent-induced differences in the chemical shifts of H(4) in **56** and H(5) in **58** are of some help (Takeuchi *et al* 1978; Nagarajan *et al* 1982a). More definitive discrimination is possible using ^{13}C NMR spectroscopy (Nagarajan *et al* 1982d). Thus, the sole proton-bearing C(4) in **56** and C(5) in **58** are readily picked up in the ^{13}C NMR spectra. The former is a doublet with a chemical shift of 131.7 ppm and $^1J_{CH}$ of 199 Hz. The latter is a doublet split further into a fine quartet: δ 122.3, $^1J_{CH}$ 200 Hz and $^3J_{CH}$ 2 Hz.

152.4 ppm, $\delta C(5)$ in 57, 121.5 ppm. In fact for a large number of isomeric pairs studied, the 5-nitroimidazoles had $\delta C(4)$ in the narrow range of 130–133 ppm and their 4-nitro counterparts had $\delta C(5)$ at 120–124 ppm. The difference is to be traced to C(4) in the former being attached to a biligant N atom and C(5) of the latter to a triligant one. ^{15}N NMR spectroscopy is also of diagnostic value in such cases (Chen *et al* 1983).

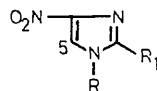
Two further points are worth noting. Both in the case of pyrazoles and imidazoles coupling of carbon atoms is not observed with protons three bonds removed, if these are located in a ring as part of an alkylene group (e.g. 10). Secondly, N-unsubstituted imidazoles and pyrazoles are capable of tautomerism and both ^{13}C (Nagarajan *et al* 1982a, 1985c) and ^{15}N (Chen *et al* 1983) NMR spectra provide equilibrium data.

In an extension of this work, we have studied the ^{13}C NMR spectra of all the three possible 1-methyl-x-nitropyrazoles 60–62 and two (63, 64) of the three possible 1-methyl dinitropyrazoles (63–65). Pertinent data are 60: C(4) δ 108.1; d $\times$ d; C(5) δ 133.2; d $\times$ q 61: C(3) δ 135.8; d $\times$ d; C(5) 129.5, d $\times$ q; 62 C(3) 137.8; d $\times$ d; C(4) 106.4, d $\times$ d (Nagarajan and Shenoy 1985) 63 C(5), δ 132.0; d $\times$ q; 64 C(3), δ 133.8, d (Nagarajan 1980).



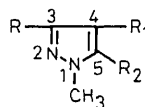
56 R = R₁ = Me

57 R = 4-NO₂-C₆H₄; R₁ = Me



58 R = R₁ = Me

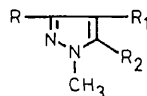
59 R = 4-NO₂-C₆H₄; R₁ = Me



60 R = NO₂; R₁ = R₂ = H

61 R = R₂ = H; R₁ = NO₂

62 R = R₁ = H; R₂ = NO₂



63 R = R₁ = NO₂; R₂ = H

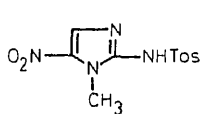
64 R = H; R₁ = R₂ = NO₂

65 R = R₂ = NO₂; R₁ = H

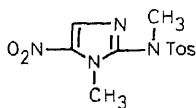
5. Imidazopyrazoles from cyclo addition reaction of a nitroimidazole and diazomethane

The unique contribution of ^{13}C NMR spectroscopy to solutions of structural problems not easily amenable to more conventional techniques is perhaps best illustrated in the complex mixture of products arising from the reaction of the toluene sulphonamido-nitroimidazole 66 with diazomethane. The formation of this bewildering array of products 67–73 (two more are not relevant for this discussion and are hence not shown) (Sudarsanam *et al* 1980; Nagarajan *et al* 1982b) with the exception of 67 has been traced to the participation of nitroimidazoline 68 in a cycloaddition reaction with the methylating agent. The isomeric N-methyl derivatives 67 and 68 were best distinguished by their ^{13}C NMR spectra: 67 C(4) δ 130.3, d, $^1J_{CH}$ 202 Hz; 68 C(4) δ 122.7; d $\times$ q; $^1J_{CH}$ 211, $^3J_{CH}$ 1.8 Hz. The pair of imidazopyrazoles 70 and 72 were similarly identified: 70: C(3) δ 120.0; d; $^1J_{CH}$ 195 Hz; 71 C(3) δ 113.4; d $\times$ q; $^1J_{CH}$ 198; $^3J_{CH}$ 3.5 Hz. Presence or

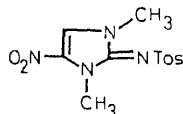
the methyl carbamoylimidazopyrazoles **71** and **73** which were artefacts in this reaction. However, chemical shifts came to our rescue: **71** $\delta C(3)$ 119.1; **73** $\delta C(3)$ 110 ppm, following the well-established pattern among the isomeric pyrazoles treated in §3. A similar profitable exercise was carried out on thiazolopyrazoles obtained by the treatment of 2-dichloroacetamido-5-nitrothiazole (Sudarsanam *et al* 1980; Nagarajan *et al* 1982b).



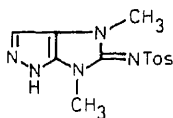
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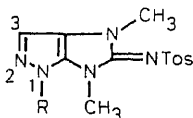
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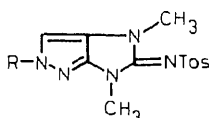


69



70 R = CH₃

71 R = CONHCH₃



72 R = CH₃

73 R = CONHCH₃

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Proton NMR studies of peptide conformations

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Abstract. This article reviews recent ^1H NMR studies on peptides carried out in the author's laboratory. Methods for the delineation of hydrogen bonded NH groups are discussed and exemplified by studies of conformationally constrained peptides. The application of concentration dependences of NMR parameters for NH groups in peptides to the study of peptide aggregation in apolar solvents is considered. Investigations on chemotactic peptide analogs and suzukacillin fragments are briefly summarized. Nuclear-Overhauser effect studies on β -sheet and β -turn conformational models are described. NMR studies on conformational transitions accompanying dissolution of single crystals are illustrated by a study of a peptide containing a -Pro-Pro- segment.

Keywords. Nuclear magnetic resonance; peptide conformation; hydrogen bonding; peptide aggregation; nuclear-Overhauser effects.

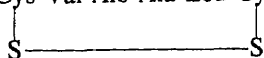
1. Introduction

The potential importance of NMR methods in determining the solution conformations of peptides was first emphasized in early studies of the cyclic decapeptide gramicidin S (Stern *et al* 1968; Wyssbrod and Gibbons 1973). In the last decade there has been an explosive increase in the use of NMR methods in peptide conformational analysis, fuelled in part, by the dramatic revolution in NMR spectroscopy, brought about by the ready accessibility of high field spectrometers and more recently, by the introduction of powerful multiple pulse methods, including two-dimensional NMR spectroscopy. The recognition of the important role of peptides in mediating a striking variety of biological processes has provided a major stimulus for these studies. While x-ray diffraction remains the method of choice for determining peptide structures in the solid state (Karle 1981; Benedetti 1982), high resolution NMR is preeminent in analysis of solution conformations (Wüthrich 1976; Deslauriers and Smith 1980). In solution, the dynamic, flexible nature of oligopeptides can result in the population of a number of conformational states, with rapid interconversions being possible, resulting in ambiguities in the interpretation of NMR parameters, in terms of specific conformations (Jardetsky 1980). The use of model peptides with limited conformations can help to define the limits of applicability of various NMR techniques and also serve to calibrate ancillary spectroscopic techniques like IR, CD and Raman methods, using the NMR results as the basis for conformational interpretations. This article briefly reviews some results obtained at Bangalore over the past few years, which illustrate the application of NMR methods to the study of the conformations and aggregation of model peptides in organic solvents.

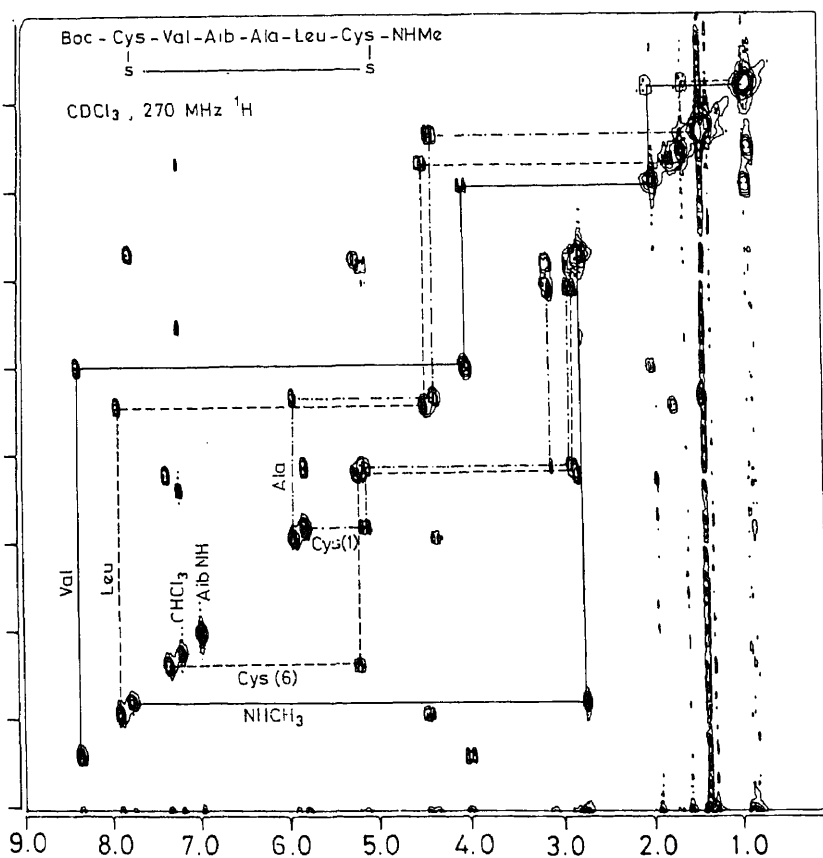
2. Assignment of resonances

^1H NMR studies of peptide conformations are contingent upon the assignment of resonances to protons (NH, C^αH , C^βH etc) on specific amino acid residues. C^βH

hydrogens on many residues can be identified unambiguously on the basis of chemical shift values (Wüthrich 1976). Sequential double resonance experiments then permit the connectivity to the $C^{\alpha}H$ and NH protons to be established. The availability of very high field NMR spectrometers (500 or 600 MHz for 1H) provides excellent resolution of complex spectra and recent two-dimensional (2D) NMR techniques permit ready assignment of specific spin systems (Benn and Gunther 1983; Bax 1982). Figures 1 and 2 exemplify the use of 2D correlated spectroscopy (cosy) (Aue *et al* 1976; Kumar *et al* 1980), in assignment of oligopeptide 1H NMR spectra. The peptide Boc-Cys-Val-Aib-Ala-Leu-Cys-NHMe was synthesized as a model for investigating



the conformations of 20-membered disulfide loops (R Kishore and S Raghothama, unpublished). Boc-Asp(OBzl)-Leu-Thr-Gly-Gly-Gly-Val-OBzl is a synthetic fragment



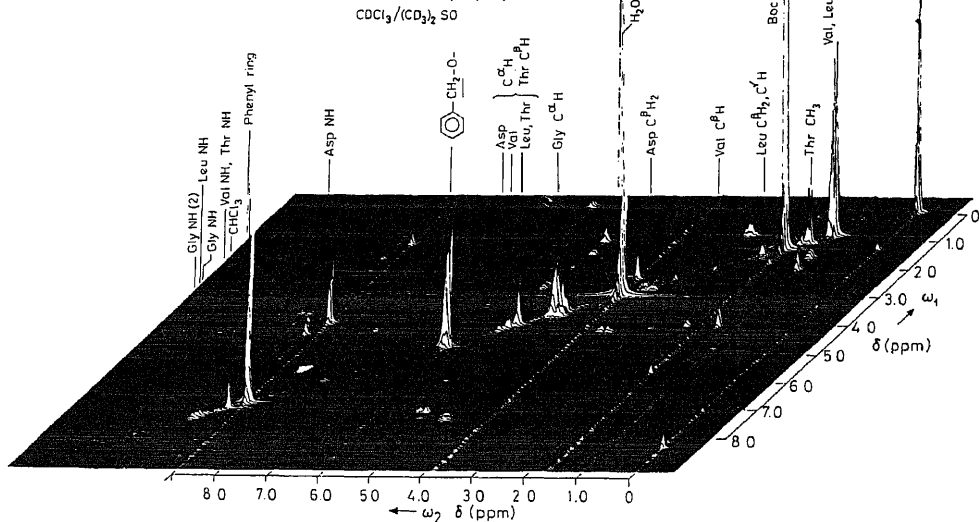


Figure 2. 270 MHz ^1H COSY spectrum (stacked plot) of Boc-Asp(Bzl)-Leu-Thr-Gly-Gly-Gly-Val-OBzl in a CDCl_3 -(CD_3) $_2\text{SO}$ mixture.

of a naturally occurring sperm activating peptide (Balaram 1984). It is clearly seen from figures 1 and 2 that the spin systems of individual amino acid residues can be discerned. In cases where the same amino acid occurs more than once in an oligopeptide, assignments of resonances to specific residues are more difficult. In favourable situations, where interresidue nuclear Overhauser effects (NOE's) are observable (*vide infra*) between adjacent amino acids in a sequence, assignments may be made to specific residues (Wagner *et al* 1981; Billeter *et al* 1982). The use of long range spin-spin couplings may also aid in tracing the sequence of amino acids in peptide chains (Wynants and Van Binst 1984). Unambiguous assignments in homooligopeptides can also be made by selective introduction of C^α -deuterated amino acids by synthesis.

3. Hydrogen bonding

Folded peptide structures are often stabilized by intramolecular $\text{C}=\text{O} \cdots \text{H}-\text{N}$ hydrogen bonds (Toniolo 1980). Typical folded conformations are illustrated in figure 3. A major objective of NMR studies of peptides is to delineate the CO and NH groups involved in intramolecular hydrogen bonding. The extent of solvent exposure of NH groups may be probed by a variety of methods. The more commonly employed techniques include the following:

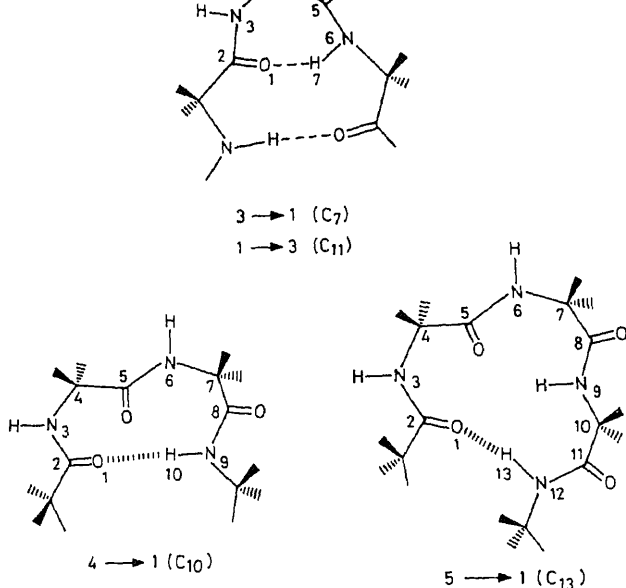


Figure 3. Representative intramolecularly hydrogen bonded conformations in peptides.

3.1 Temperature coefficients of chemical shifts

Temperature dependence of NH chemical shifts are usually measured in polar hydrogen bonding solvents like dimethylsulphoxide (DMSO), methanol (MeOH) or water. NH resonances generally move *upfield* with increasing temperature, reflecting breaking of solute-solvent hydrogen bonds. Temperature dependences are invariably linear and the temperature coefficient ($d\delta/dT$) values have been used to characterize solvent exposed and shielded NH groups. $d\delta/dT$ values < 0.003 ppm/K in solvents like DMSO are characteristic of solvent shielded (presumably intramolecularly hydrogen bonded NH groups), while values > 0.005 ppm/K are typical of solvent exposed (free) NH groups (Kopple *et al* 1969; Hruby 1974; Venkatachalapathi and Balaram 1981a). Intermediate $d\delta/dT$ values are more difficult to interpret definitively and have sometimes been taken as indicative of weakly intramolecularly hydrogen bonded NH groups (Ravi *et al* 1983). Temperature dependences in aromatic solvents have also proved useful in delineating different kinds of NH groups, probably due to specific solvation of the peptide moiety by these solvents (Venkatachalapathi and Balaram 1981a). $d\delta/dT$ values in apolar solvents like chloroform, cannot distinguish between intramolecularly hydrogen bonded and free NH groups, but can be diagnostic of intermolecular association (Stevens *et al* 1980; Iqbal and Balaram 1982a).

3.2 Solvent perturbation effects

In this method, changes in chemical shifts of NH resonances are monitored on addition of a strongly hydrogen bonding solvent, like MeOH or DMSO, to a peptide solution in a poorly hydrogen bonding solvent like CHCl_3 or $\text{CF}_3\text{CH}_2\text{OH}$. Exposed NH groups

show large downfield shifts in such a solvent titration experiment, whereas shielded NH groups are significantly less affected (Pitner and Urry 1972). Monotonic changes in δ values on altering solvent composition are indicative of the absence of solvent-induced structural changes. Conversely, sharp discontinuities are suggestive of conformational transitions.

3.3 Paramagnetic radical-induced line broadening

The addition of stable organic free radicals like nitroxides, can induce line broadening of solvent exposed NH groups by enhancement of relaxation rates (Kopple and Schamper 1972; Kopple and Zhu 1983). This experiment is best carried out in apolar solvents like CHCl_3 , where the solvent does not compete extensively with the radical for interaction with NH groups.

3.4 Rates of hydrogen deuterium (H-D) exchange

Solvent-exposed NH groups show much greater rates of H-D exchange as compared to shielded NH groups (Stern *et al* 1968; Narutis and Kopple 1983). This experiment is particularly informative in pure solvent systems like CD_3OD , D_2O etc. In mixed solvent systems quantitative interpretations are risky.

3.5 Transfer of saturation from solvent resonances

In this technique intensity changes in peptide NH resonances are monitored while the exchangeable proton of the solvent is saturated. Intensities of solute resonances originating from exposed and labile hydrogens are diminished by transfer of saturation, due to rapid exchange with the solvent, whereas resonances of 'buried' hydrogens are less affected (Glickson *et al* 1974).

In all the methods considered above a clear distinction *cannot* be made between intramolecularly hydrogen-bonded and sterically shielded NH groups. In peptides lacking unusual structural features, solvent shielded NH groups are frequently considered to be hydrogen-bonded. In conformationally flexible peptides interpretations of such hydrogen bonding studies are often inconclusive. The power of these methods is best illustrated in studies of conformationally constrained peptides.

Figure 4 illustrates the temperature and solvent dependence of NH chemical shifts in the decapeptide Boc-Aib-Pro-Val-Aib-Val-Ala-Aib-Ala-Aib-OMe. Nine well-resolved NH resonances can be seen at 270 MHz (Iqbal and Balaram 1981a). The data in figure 4 clearly establish that with the exception of one Aib NH group (assigned by virtue of its high field position in CDCl_3 to the N-terminal urethane) all other 8 NH groups are solvent-shielded or hydrogen-bonded. Of these one (Aib NH(S_2)) is probably involved in a weaker interaction. These observations, together with the known stereochemical propensity of Aib residues to favour 3_{10} helical structures (Nagaraj and Balaram 1981; Prasad and Balaram 1984) led to the suggestion of the hydrogen bonding scheme shown in figure 5 (Iqbal and Balaram 1981a). The interpretation of the NMR results was well supported by the results of a crystal structure determination (figure 5) (Francis *et al* 1983). Analysis of hydrogen-

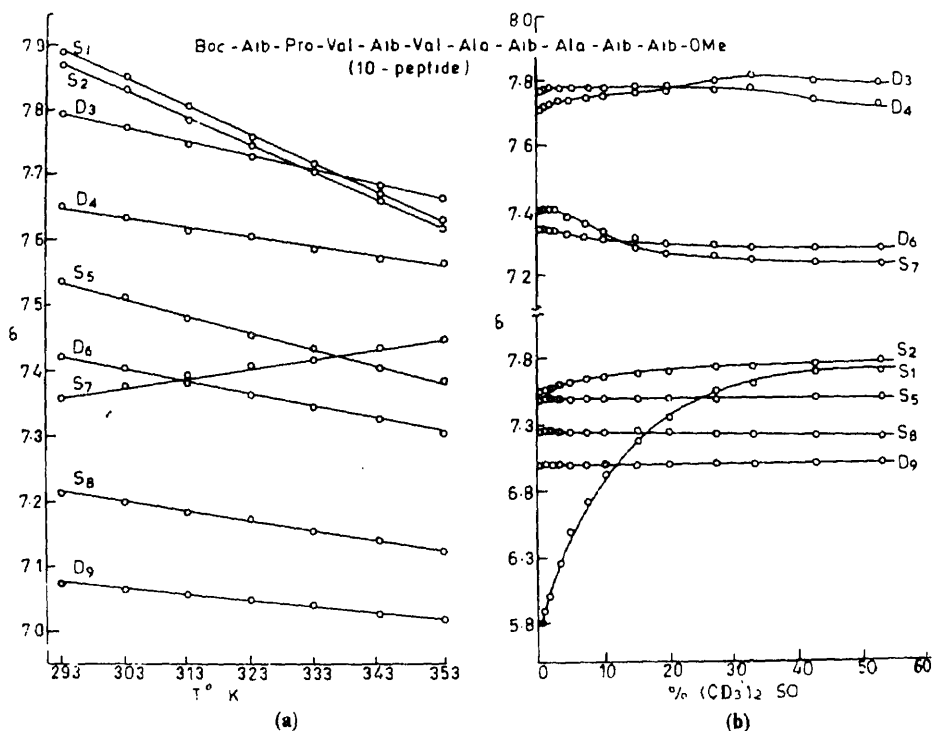
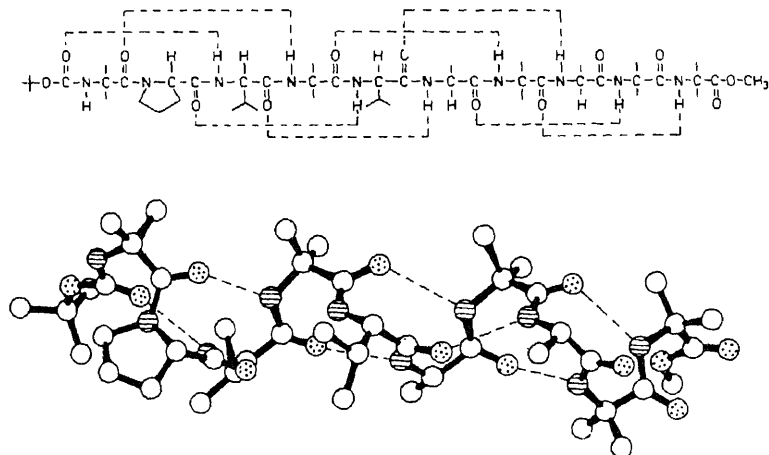


Figure 4. (a) Temperature dependence of NH chemical shifts in the decapeptide Boc-Aib-Pro-Val-Aib-Val-Ala-Aib-Ala-Aib-Aib-OMe in (CD₃)₂SO. S_m, D_n refer to singlet and doublet NH resonances. The subscript *n* refers to the order of appearance from low field in (CD₃)₂SO. (b) Dependence of NH chemical shifts on solvent composition in CDCl₃-(CD₃)₂SO mixtures (from Iqbal and Balaram 1981a).



16 residues (Iqbal and Balaram 1981b, 1982b) and a wide variety of peptide conformational models (Venkatachalapathi and Balaram 1981b; Ravi and Balaram 1984).

4. Peptide aggregation

The concentration dependence of ^1H NMR parameters of NH groups can provide valuable information about the intermolecular association of peptides, in solution. Peptide aggregation in apolar solvents like chloroform is often mediated by intermolecular hydrogen bond formation. The possible role of peptide backbone conformation on ease of aggregation has been illustrated in a study of two chemotactic peptide analogs, Formyl-Met-X-Phe-OMe ($X = \text{L-Leu, Aib}$). In the $X = \text{Leu}$ peptide no evidence has been obtained for a folded conformation in CDCl_3 or $(\text{CD}_3)_2\text{SO}$. On the contrary in the $X = \text{Aib}$ peptide the Phe NH is involved in an intramolecular hydrogen bond, suggesting either a C_7 (γ -turn) conformation centred at Aib or a Met-Aib β -turn (Raj and Balaram 1985). Similar conformations were earlier considered for the analog For-Met-Aib-Phe-OH (Iqbal *et al* 1984). Figure 6 shows the concentration dependence

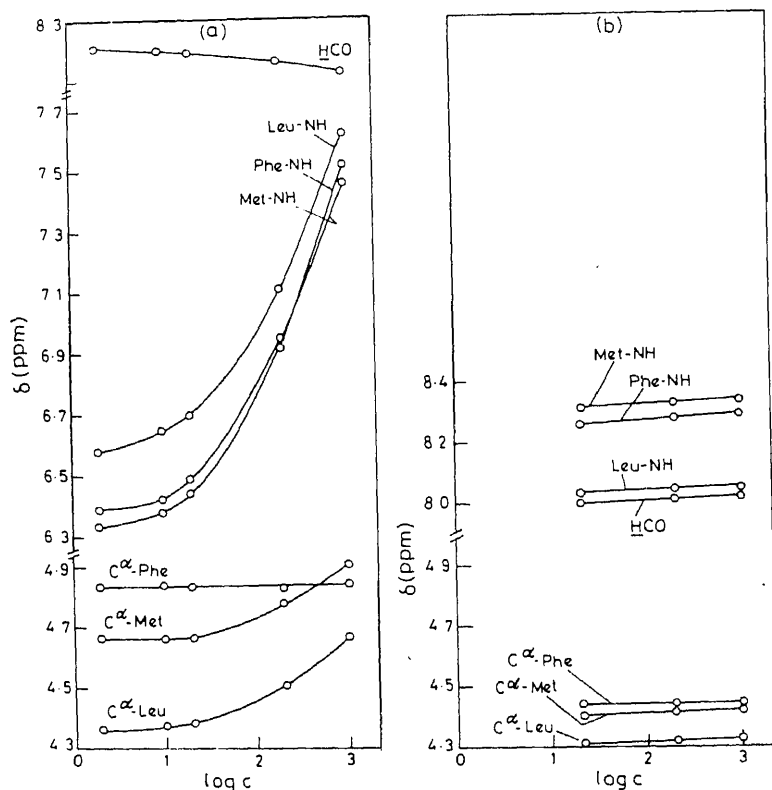
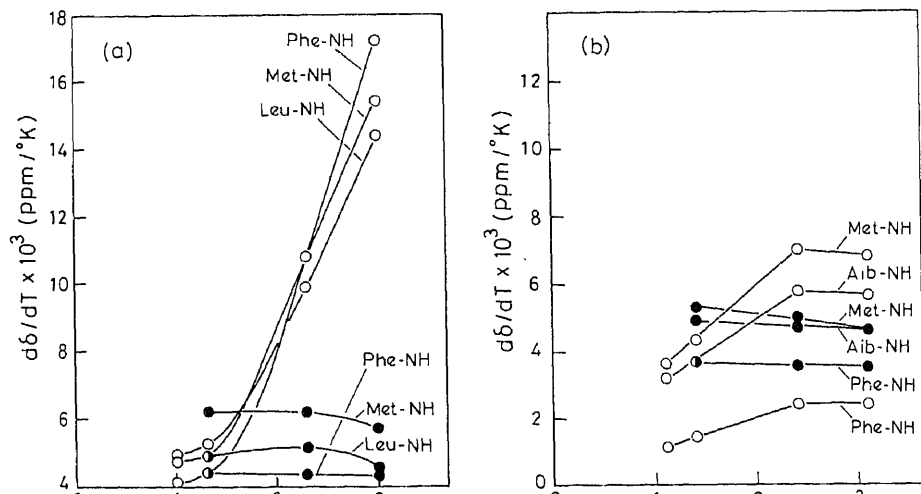


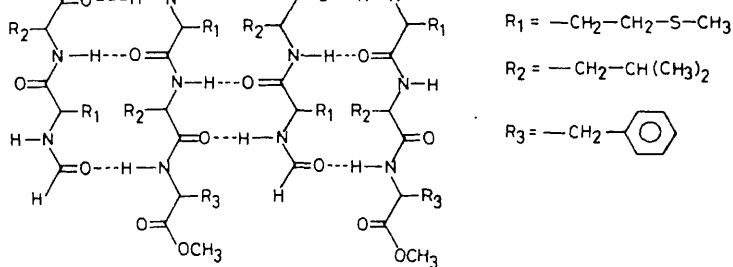
Figure 6. Concentration dependence of chemical shifts (δ) for various resonances in Formyl-Met-Leu-Phe-OMe in CDCl_3 (a) and $(\text{CD}_3)_2\text{SO}$ (b). Abscissa expresses concentration as $\log c$, where c is molar concentration of peptide $\times 10^4$ (from Raj and Balaram 1985).

of the chemical shifts of NH resonances in Formyl-Met-Leu-Phe-OMe in CDCl_3 and $(\text{CD}_3)_2\text{SO}$. The concentration dependence of temperature coefficients ($d\delta/dT$ values) for both peptides in CDCl_3 and $(\text{CD}_3)_2\text{SO}$ are summarized in figure 7. The data strongly suggest that both peptides are unassociated in $(\text{CD}_3)_2\text{SO}$ but are aggregated in CDCl_3 . All three NH groups show large concentration effects in the X = Leu peptide, compatible with the aggregation mode illustrated in figure 8. In the X = Aib case the folded peptide aggregates involve only the exposed Met and Aib NH groups in intermolecular hydrogen bonding.

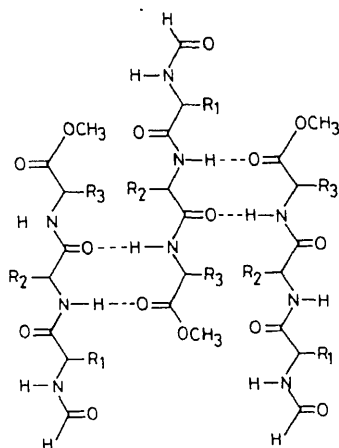
The possible application of such studies is further illustrated by a comparison of the peptides Boc-X-Aib-Leu-Aib-Gly-Leu-Aib-Pro-Val-Aib-Aib-OMe (X = Gln 11G, X = Ala 11A). Peptide 11G forms the 7–17 segment of the channel forming ionophore, suzukacillin. In order to evaluate the role of the lone Gln residue in promoting peptide association in apolar solvents, which model membrane environments, the NMR parameters of peptides 11A and 11G were compared.

In peptide 11G nonlinear temperature dependences of chemical shifts are observed for a few NH groups including the Gln sidechain carboxamide protons (figure 9). The nonlinearity is particularly pronounced for the lone Gly NH (T_2) resonance in $(\text{CD}_3)_2\text{SO}$ at low concentration. A striking feature of the data for the Ala peptide 11A is the absence of such nonlinear behaviour (figure 10). A detailed analysis of the concentration and solvent dependence of NH chemical shifts has permitted the development of a model which ascribes an important role to the Gln sidechain in both intermolecular hydrogen bonding and intramolecular sidechain-backbone interactions (Iqbal and Balaram 1981c). The use of concentration dependences of $d\delta/dT$ values in evaluating the mode of peptide self-association has been described in related studies of a helical decapeptide (Iqbal and Balaram 1982a).

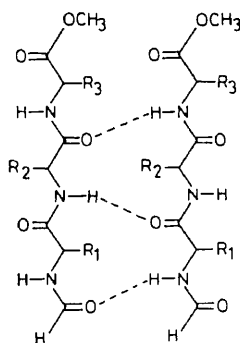




(a)



(b)



(c)

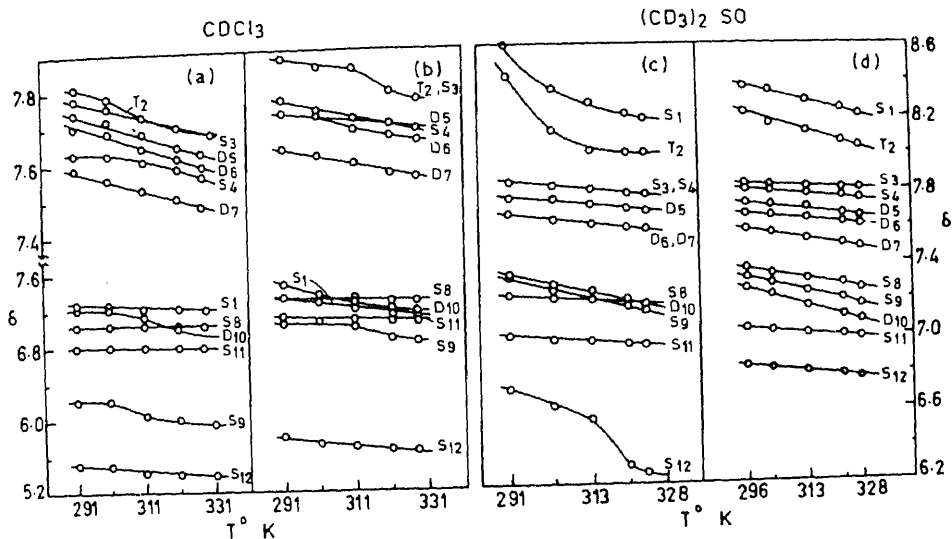
Figure 8. Schematic representation of aggregation modes for Formyl-Met-Leu-Phe-OMe in chloroform, consistent with NMR data. (a) antiparallel β -sheets 'in register'. (b) antiparallel β -sheets 'out register'. (c) parallel β -sheet aggregates.

5. Nuclear-Overhauser effects

Proton-proton NOE's can establish spatial proximity of hydrogen atoms in organic molecules (Noggle and Schirmer 1971; Bothner-By 1979). NOE's are generally observable when the interproton distance is $\leq 3.0 \text{ \AA}$. Useful interproton distances in studies of peptide conformation are indicated in figure 11. NOE magnitudes are dependent on the correlation time (τ_c) modulating the proton-proton dipolar interaction (Solomon 1955) and are given by the equation

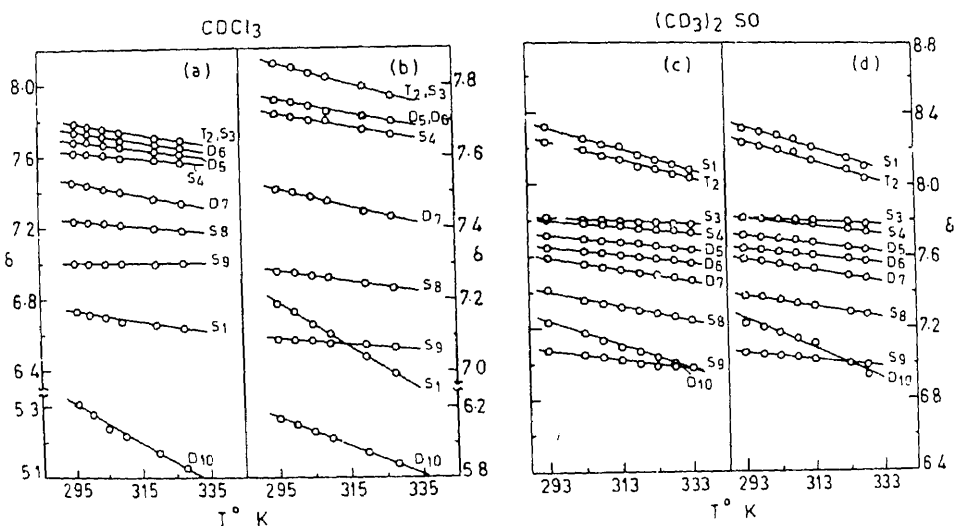
$$f_I(S) = \frac{5 + \omega^2 \tau_c^2 - 4\omega^4 \tau_c^4}{10 + 23\omega^2 \tau_c^2 + 4\omega^4 \tau_c^4}, \quad (1)$$

where $f_I(S)$ is the fractional enhancement in resonance intensity of spin S when spin I is



TEMPERATURE DEPENDENCE OF NH CHEMICAL SHIFTS IN 11-G
(a) 0.00086 M, (b) 0.043 M, (c) 0.00086 M, (d) 0.043 M

Figure 9. Temperature dependence of NH chemical shifts in the suzukacillin 7-17 fragment Boc-Gln-Aib-Leu-Aib-Gly-Leu-Aib-Pro-Val-Aib-Aib-OMe (11-G). (a) CDCl₃, 0.00086 M peptide. (b) CDCl₃, 0.043 M. (c) (CD₃)₂SO 0.00086 M. (d) (CD₃)₂SO 0.043 M.



-TEMPERATURE DEPENDENCE OF NH CHEMICAL SHIFTS IN 11-A
(a) 0.0018 M, (b) 0.045 M, (c) 0.0018 M, (d) 0.045 M

Figure 10. Temperature dependence of NH chemical shifts in the peptide Boc-Ala-Aib-Leu-Aib-Gly-Leu-Aib-Pro-Val-Aib-Aib-OMe (11-A). (a) CDCl₃, 0.0018 M peptide. (b) CDCl₃, 0.045 M. (c) (CD₃)₂SO 0.0018 M. (d) (CD₃)₂SO 0.045 M.

saturated, ω is the Larmor precession frequency and τ_c is the rotational correlation time, which randomizes the orientation of the internuclear vector ($I - S$) (Balaram *et al* 1972, 1973). As a consequence of equation (1) NOE's are sharply dependent on τ_c in the region $\omega\tau_c \sim 1$ (figure 12). While positive NOE's are observed in small molecules at all

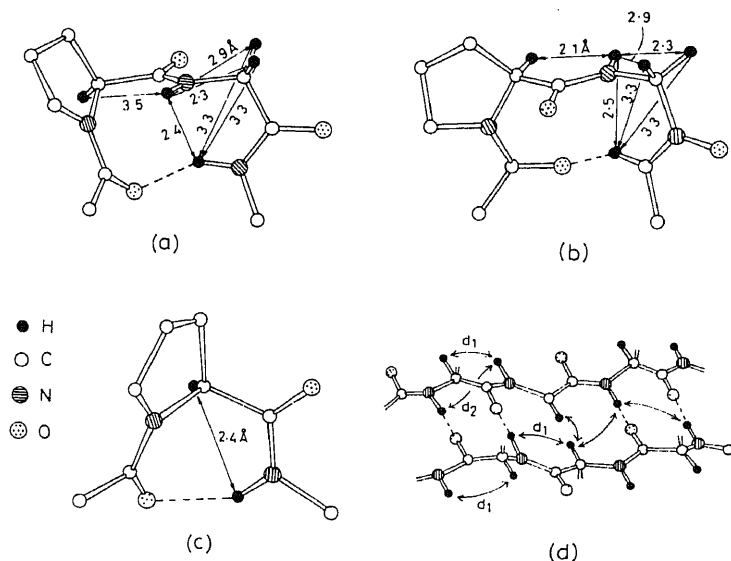


Figure 11. Interproton distances in idealized peptide conformations. (a) Pro-Gly type I β -turn. (b) Pro-Gly type II β -turn. (c) γ -turn (C_7) conformation. (d) Antiparallel β -sheet conformation. d_1 ($C_1H-N_{i+1}-H$) is generally 2.2–2.4 Å and gives rise to large NOEs. d_2 and d_3 are generally ≥ 3.0 Å in this structure. Transannular NOEs are weak but observable (Kuo and Gibbons 1980; Billeter *et al* 1982; Wagner *et al* 1981).

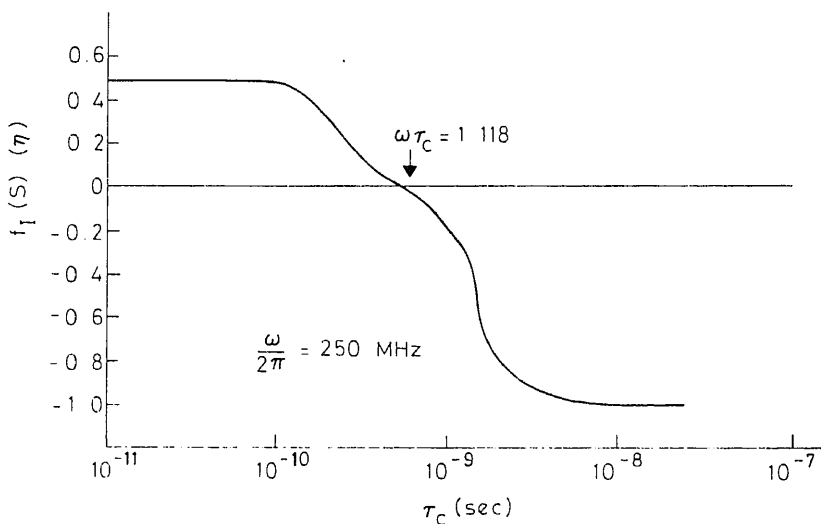


Figure 12. Dependence of 1H - 1H NOE magnitude (η) on the correlation time τ_c (from

available resonance frequencies, NOE's in macromolecules are generally negative. In oligopeptides both positive and negative NOE's are observed depending on the precise values of τ_c and the spectrometer frequency employed (Glickson *et al* 1976). In unfavourable cases where $\omega\tau_c \sim 1$, NOE magnitudes can be very small making experimental detection difficult. Nevertheless different NOE studies have provided some of the clearest evidence for folded peptide conformations (Rao *et al* 1983; Kuo and Gibbons 1980; Bothner-By 1979).

Illustrative difference NOE experiments on model β -turn peptides, Piv-Pro-X-NHMe are shown in figure 13. Type II β -turns (*e.g.* X = D-Ala, D-Leu, D-Val) are readily recognized by a large NOE between the X-NH and Pro C α H protons. These studies have

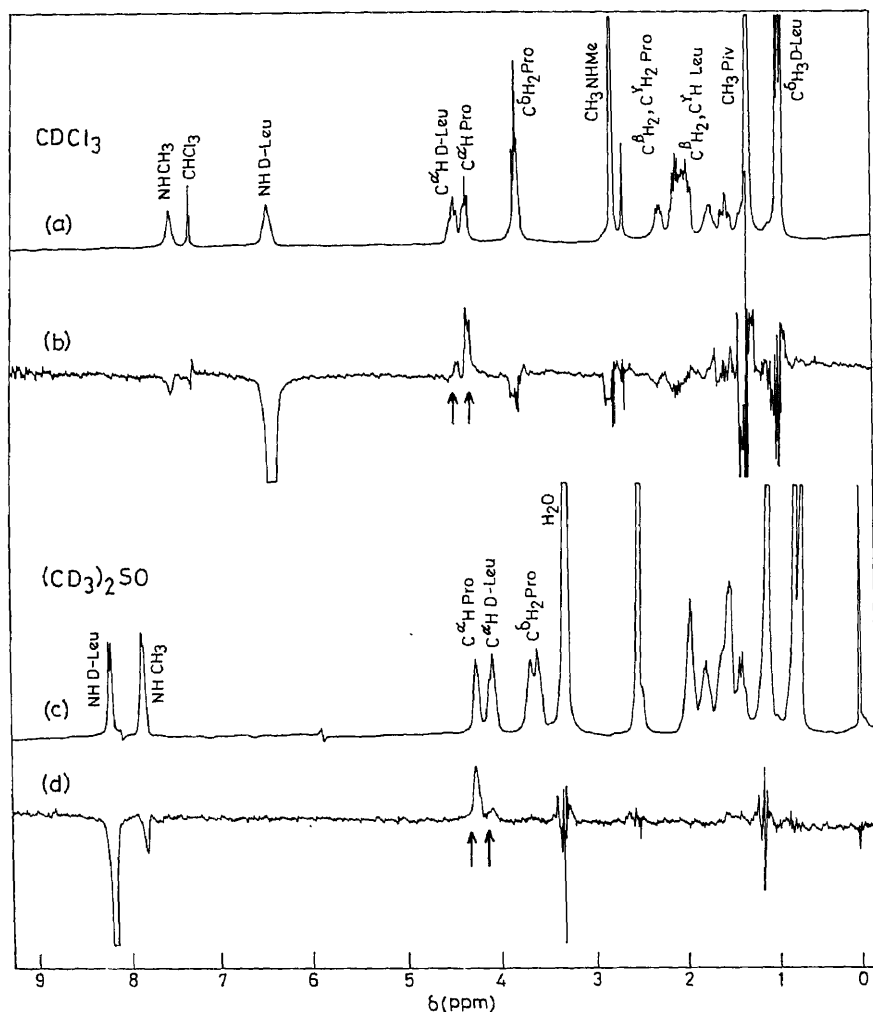


Figure 13. 270 MHz ^1H NMR spectra of Pivaloyl-Pro-D-Leu-NHMe in (a) CDCl_3 and (c) $(\text{CD}_3)_2\text{SO}$. (b) Difference NOE spectrum ($\times 16$) in CDCl_3 on saturation of D-Leu NH. Note partial saturation of NHCH_3 . (d) Difference NOE spectrum ($\times 4$), in $(\text{CD}_3)_2\text{SO}$ on saturation of D-Leu NH. Note partial saturation of NHCH_3 . Arrows indicate observed NOE's (from

permitted a detailed analysis of various β -turn conformations and have aided in the development of correlations with circular dichroism (CD) approaches (Rao *et al* 1983). The potential utility of NOE methods in identifying β -sheet conformations is exemplified by studies on a cyclic hexapeptide disulphide (figures 14, 15). Most relevant interresidue NOE's have been observed, confirming the antiparallel β -sheet conformation, suggested by conventional NMR studies (R Kishore and S Raghothama, unpublished). Extensive NOE studies on several oligopeptides, carried out in this laboratory, suggest that even in hexapeptides NOE magnitudes are sensitive to solvent viscosity and negative NOE's are sometimes observed. In the case of the hexapeptide disulphide mentioned above, negligible NOE's could be detected in DMSO at 20°C. However, heating to 40°C resulted in the observation of small positive NOE's, clearly establishing a correlation time (τ_c) dependence. The routine use of NOE analysis in longer oligopeptides has been greatly facilitated by the development of 2D-NOE spectroscopy (NOESY) (Kumar *et al* 1980; Wider *et al* 1984).

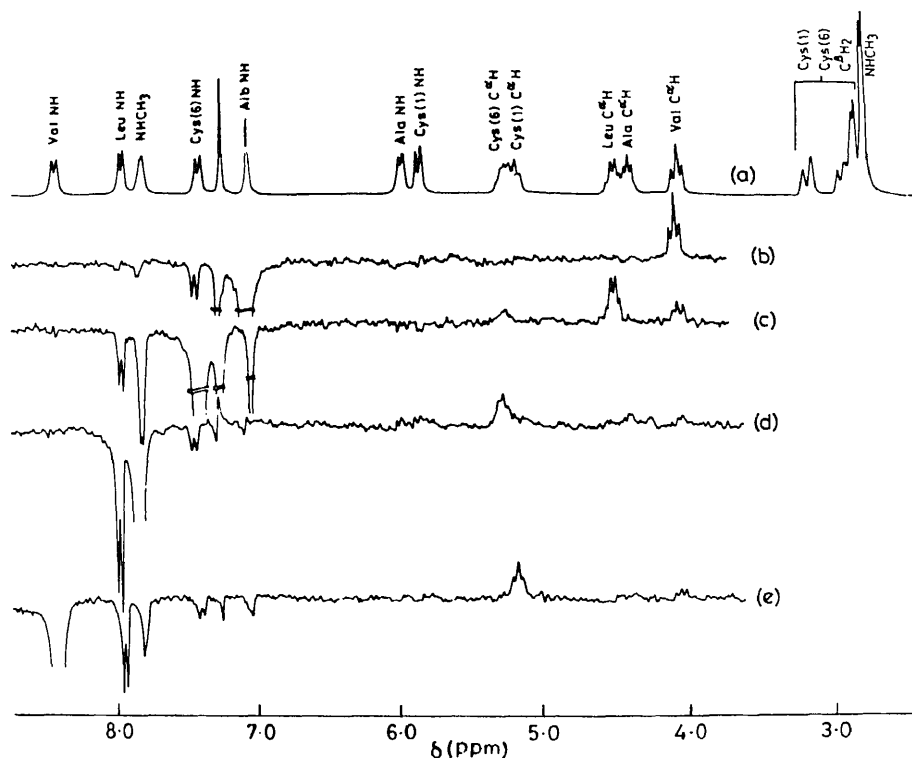


Figure 14. (a) Partial 270 MHz ^1H NMR spectrum of Boc-Cys-Val-Aib-Ala-Leu-Cys-



NHMe in CDCl_3 (b)–(e) Difference NOE spectra ($\times 16$) obtained by saturation of specific NH resonances. The saturated peak appears as an intense negative signal in the difference

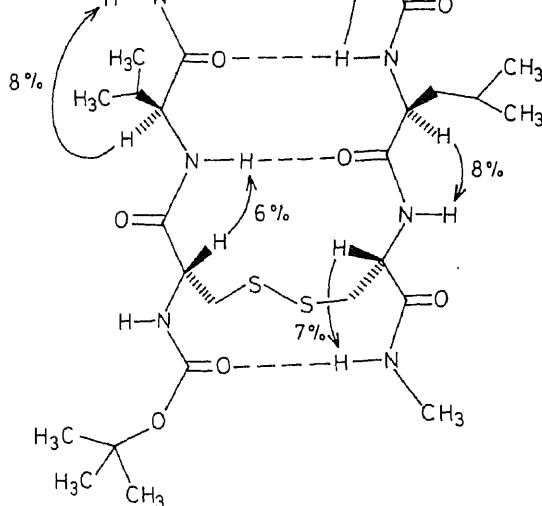


Figure 15. Antiparallel β -sheet conformation of Boc-Cys-Val-Aib-Ala-Leu-Cys-NHMe



consistent with NMR data. Observed NOE's are indicated by arrows linking the two protons. Arrow head indicates irradiated proton.

6. Spin-spin coupling constants

The value of the vicinal coupling constant ($J_{\text{HNC}\alpha\text{H}}$) in aminoacid residues is related to the dihedral angle about the $\text{N}-\text{C}^\alpha$ bond (ϕ) by the well-known Karplus relationship (Bystrov 1976). A single value of J is compatible with as many as 4 ϕ values leading to ambiguities in interpretation. The combined use of theoretical energy calculations in conjunction with NMR J values can reduce this degeneracy (Gibbons *et al* 1970). Conformational averaging can further influence observed J values, obscuring the stereochemical information (Jardetsky 1980). Despite these difficulties $J_{\text{HNC}\alpha\text{H}}$ values have been widely used in parallel with other NMR methods. $^3J_{\text{HH}}$ values of 6–8 Hz have been obtained for residues, where dynamic averaging is likely and also for residues in rigid helical conformations (Iqbal and Balaram 1981a). Large values of $^3J_{\text{HH}}$ (≥ 9 Hz) have been observed for peptides in rigid extended β -sheet conformations (Kishore and Balaram 1984). Attempts to use both geminal ($^2J_{\text{HH}}$) and $^3J_{\text{HH}}$ values to obtain both ϕ and ψ values for Gly residues in peptides have been reported (Barfield *et al* 1976). The use of heteronuclear vicinal coupling constants (*e.g.* $-\text{HC}-\text{CO}-^{15}\text{N}-$ and $^{13}\text{CO}-\text{N}-\text{C}-\text{H}$) further expands the possible utility of J values as probes of peptide conformation (Fischman *et al* 1980).

7. Conformational changes on dissolution of single crystals

^1H NMR studies of peptide structures in solution are often complicated by the presence of multiple conformational states and the attendant problems of dynamic averaging. A direct comparison with the results of crystal structure determinations is often difficult, since x-ray studies invariably yield only a single solid state conformation. It is thus important to establish the nature of the conformational transitions, which accompany dissolution of single crystals. This problem has been addressed in a study of the model peptide, Boc-Aib-Pro-Pro-NHMe. The presence of a Pro-Pro segment can lead, in principle, to various low energy conformational states, of which four are illustrated in figure 16. These correspond to distinct conformations about the Pro-Pro peptide bond (ω) and the Pro(2) C^α -CO (ψ) bond. Single crystals of the peptide were obtained and an x-ray diffraction study yielded the following conformational angles for the Pro-Pro segment: Pro(2) $\omega = 178.7^\circ$ (173.2°), $\phi = -71.3^\circ$ (-67.0°), $\psi = 158.1^\circ$ (157.1°); Pro(3) $\omega = 179.5^\circ$ (172.1°), $\phi = -71.8^\circ$ (-62.3°), $\psi = 148.6^\circ$ (154.4°), where values in parentheses correspond to the second molecule in the crystallographic asymmetric unit (Balaram *et al* 1983). These values correspond to a *trans* Pro-Pro peptide bond, with a *trans'* conformation at the C^α -CO (ψ) bond of Pro(2).

Figure 17 shows a 270 MHz ^1H NMR spectrum of the peptide obtained by dissolving *single crystals* in precooled CDCl_3 at 233 K. Resonances due to a single conformation are observed, which must correspond to the *trans-trans'* Pro(2) conformation observed by x-ray diffraction in the solid state. On warming, additional resonances appear, which correspond to population of the *cis* conformer about the Pro-Pro bond and the *cis'* conformer about the Pro(2) C^α -CO bond. Figure 17 illustrates the appearance of as many as three conformers, as observed from the methyl resonance of the N-methylamide group. It is clearly seen that at temperature > 293 K conformers **II** and **III** go into rapid exchange suggestive of a fast equilibration about the Pro(2) C^α -CO bond. This is consistent with a lower barrier for rotation about the C^α -CO (ψ) bond as compared to the Pro-Pro peptide (ω) bond. A 270 MHz ^1H NMR spectrum of a *non-crystalline* sample shows the presence of all three conformers at 233 K (figure 17). This

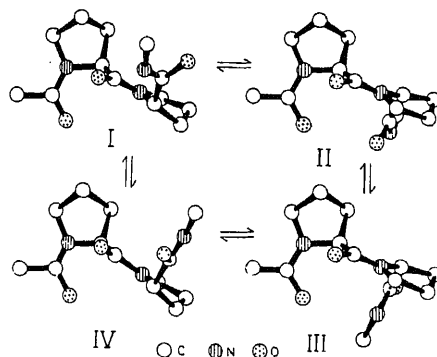


Figure 16. Perspective view of the low energy conformations of a Pro-Pro sequence. Calculations were performed on the model Ac-Pro-Pro-NHMe. **I** (*trans-trans'*); **II** (*cis-trans'*); **III** (*cis-cis'*); **IV** (*trans-cis'*). *Trans* and *cis* refer to the $\omega = 180^\circ$ and $\omega = 0^\circ$ conformations about the Pro-Pro bond respectively. *Trans'* and *cis'* refer to conformations in the ψ bond.

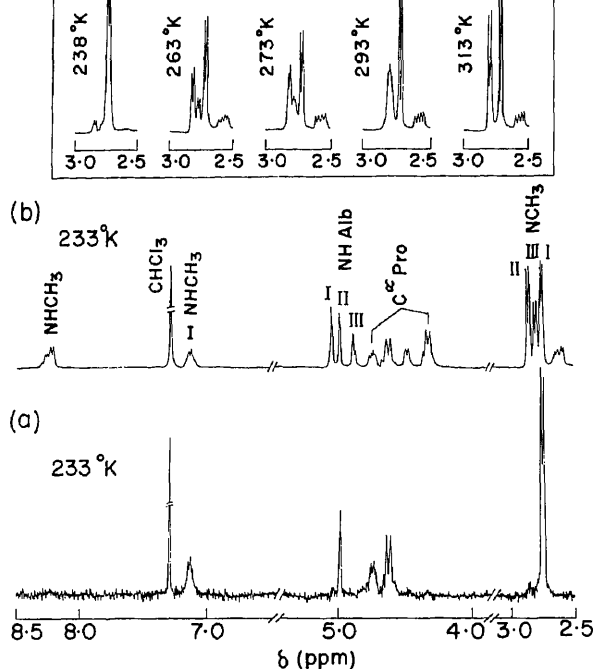


Figure 17. (a) Low temperature 270 MHz ^1H NMR spectrum of single crystals of Boc-Aib-Pro-Pro-NHMe recorded immediately after dissolution in CDCl_3 , pre-cooled in liquid N_2 and transferred to the probe at 233 K. (b) Low temperature 270 MHz ^1H NMR spectrum of a noncrystalline sample of Boc-Aib-Pro-Pro-NHMe at 233 K in CDCl_3 . (Inset) Methylamide CH_3 resonances (doublets) in Boc-Aib-Pro-Pro-NHMe. The sample was prepared as in (a) and the spectra recorded at various temperatures. I, II, III indicate an assignment to the Pro-Pro conformers described in figure 16 (from Balaram *et al* 1983).

is the first example of the observation of such transitions on dissolution of single crystals of an oligopeptide (Balaram *et al* 1982, 1983).

The studies described above provide a personalized account of ^1H NMR studies of peptide conformations, exemplified by problems investigated in the author's laboratory. No attempt has been made to review the burgeoning literature in this area. It is however clear that ^1H NMR studies provide the most powerful means of probing the structures and dynamics of peptides in solution.

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Research efforts in this area have been made possible by the active participation of a large number of collaborators, who are acknowledged in the references and in the text

in the case of unpublished work. In particular, the author wishes to thank Dr Anil Kumar, Dr C L Khetrapal and the staff of the Sophisticated Instruments Facility, Bangalore for their help over the past several years. Continued financial support from the Department of Science and Technology is gratefully acknowledged.

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Observation of a plastic crystalline phase in solid MBBA

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Abstract. Wideline and high resolution NMR studies have been carried out in MBBA in its isotropic, nematic and solid phases. Isotropic and nematic spectra correspond to what has been reported earlier. In the solid phase, contrary to expectations, very intense narrow signals similar to signals of the isotropic phase have been observed for the first time at temperatures close to the solid $\leftrightarrow$ nematic phase transition temperature. This indicates rapid reorientational or translational motion in the system. X-ray results however confirm the existence of translational order. The results are interpreted as indicative of the existence of a plastic crystalline phase in MBBA.

Keywords. Liquid crystals; MBBA; plastic crystals; nuclear magnetic resonance.

1. Introduction

The mesomorphic and solid state polymorphic behaviour of liquid crystals $nO \cdot m$ ($C_nH_{2n+1}O \cdot PhCHNPhC_mH_{2m+1}$) series of compounds have recently attracted a great deal of attention (Leadbetter *et al* 1979). In particular, the compound 10-4 (N-*p*-methoxybenzylidene-*p*-*n*-butylaniline-MBBA) has been shown to exhibit complex polymorphic behaviour below its 'melting temperature' of 22°C. Through adiabatic calorimetry, Mayer *et al* (1972) and Janik *et al* (1975), measured the temperature dependence of the specific heat of MBBA and interpreted their results as indicative of the existence of a metastable crystalline state in addition to a stable crystalline state and a glassy nematic phase (Kumagai *et al* 1981). X-ray powder pattern of Lydon and Kessler (1975) show anomalous behaviour around 15°C, in that the diffraction peak at $2\theta = 5.2^\circ$ gains intensity before finally losing it. The authors offer two possible explanations for this behaviour, in terms of (a) a monotropic metastable crystal $\rightarrow$ nematic transition followed by the formation of the stable crystalline form, or (b) the possibility of a monotropic smectic phase and the nematic phase. A large number of other experimental investigations such as calorimetry and dielectric studies (Moscicki *et al* 1977), infrared (Janik *et al* 1973; Kirov and Simova 1973) and Raman spectroscopy (Borer *et al* 1971; Vergoten 1972; Destrade and Gasparoux 1975; Arendt *et al* 1981), positron life-time measurements (Walker 1978; Jain and Kafle 1980), neutron diffraction (Dolganov *et al* 1980), ESR spin probe (Spielberg and Gelerinter 1982; Stillman *et al* 1978) and some NMR studies (Kronberg and Gilson 1977; Heinze *et al* 1978; Heinze and Grande 1978; Froix and Pochan 1978; Ito *et al* 1981; Kumagai *et al* 1981) have been directed towards understanding the nature of the polymorphism in

MBBA. Even though there is general agreement among these reports regarding the occurrence of a number of distinct phases in solid MBBA, the nature of these phases is not yet unambiguously established.

We undertook wideline proton NMR studies at ambient pressure and under high hydrostatic pressure, high resolution NMR and x-ray powder diffraction studies of MBBA to clarify its rather complex behaviour below its nematic phase. The analysis of these results presented below lead us to the conclusion that MBBA exhibits a plastic crystalline state just below its nematic phase. To the best of our knowledge this is the first report of the occurrence of a plastic crystalline phase in a substance which also exhibits liquid crystalline order. A preliminary account of this work has been published earlier (Arumugam *et al* 1983).

2. Experimental

2.1 Sample

MBBA has the tendency to absorb moisture and decompose into anisaldehyde and *p*-butylaniline (Denat *et al* 1973) and the nematic to isotropic transition temperature (T_{NI}) decreases drastically in the presence of such molecules. In the present studies MBBA was repeatedly distilled under vacuum of about 0.1 torr. The experiments were all carried out almost immediately after the distillation after sealing the sample in a tube. The temperature T_{NI} for the sample was 45.8°C and was measured both by DSC and proton NMR. Further distillation did not increase the transition temperature T_{NI} .

2.2 Wideline NMR

Wideline NMR experiments were performed at 10 MHz using a home-made oscillator-detector system with a Varian magnet. Temperature variation was carried out by passing cold nitrogen gas through a glass Dewar wherein the sample was kept. Above the room temperature, the nitrogen gas was heated and passed on to the sample. One junction of the copper-constantan thermocouple was kept right inside the sample and the other junction in a reference ice-bath. Very low amplitude for modulation was used to avoid modulation broadening and it was possible to see in the spectrum the structure at the centre of the signal in the nematic phase. For studies at high pressures a beryllium-copper (Be-Cu) lock-nut type (Ramanathan and Srinivasan 1978) pressure vessel which can withstand a pressure of 14 kbars was used. The sample was kept inside a teflon tube which was placed inside the radio frequency coil which in turn was kept in another teflon tube. The space was filled with silver chloride which acted as a pressure transmitting medium. Pressure experiments were carried out upto 5 kbars. At ambient pressure, only the smaller teflon tube was used, wherein the sample was transferred quickly and tightly sealed so that no moisture could get in. In these experiments the accuracy in temperature measurement was $\pm 1^\circ\text{C}$. To start with, the experiment was

67.89 and 41.44 MHz respectively. Both ^{13}C and ^1H spectra were recorded with broadband decoupling of proton resonances being employed. A sample tube (5 mm dia.) was used for recording ^1H spectra and a 10 mm dia sample tube was used for recording ^2H and ^{13}C spectra. Temperature variation was carried out using Bruker B-ST 100/700 temperature controller. The readings of the controller were also calibrated by directly measuring the sample temperature in a separate experiment. The accuracy in measuring the temperature was $\pm 1^\circ\text{C}$. The experiments were carried out in the isotropic phase, nematic phase and below the nematic phase down to -60°C .

3. Results

3.1 NMR studies

In the wideline NMR experiment, first the sample was heated to 48°C and the PMR spectrum corresponding to the isotropic phase was observed. The sample was cooled slowly and just below the isotropic $\leftrightarrow$ nematic transition wings started appearing and these wings were moving out on further cooling the sample. These observations are in accordance with the results reported earlier (Lee *et al* 1973). While cooling, the wings were present down to 13°C . Further cooling of the sample resulted in the sudden appearance of a sharp signal at the centre and the disappearance of the wings. Proceeding further, it was observed that the intensity of the central sharp signal reduced drastically down to -5°C and slowly thereafter and finally disappeared at -40°C . With higher modulation it could be observed with a much reduced intensity on a broad background signal. At -68°C even this disappeared completely and further cooling of the sample resulted in broadening of the entire signal. Figure 1 shows the wideline NMR spectra recorded in the isotropic and nematic phases and at temperatures just below and well below the nematic phase. While heating from -196°C the strong sharp signal appeared again and was present till 19°C . Above this temperature this disappeared and signal, characteristic of nematic phase, appeared. These results are quite unexpected since the solid phase being an ordered phase all translational motions are expected to freeze. Consequently the NMR line is expected to be broader in the solid phase than in the nematic phase due to increased dipolar couplings. However, the observation in the solid phase of an intense sharp line and the absence of wings which were present in the nematic phase indicates that in the phase below the nematic phase there is a high degree of reorientational motion of the molecules.

When MBBA was subjected to 1.5 kbar of hydrostatic pressure, the sharp signal which appeared at low temperature and at ambient pressure, appeared at room temperature itself. The nematic and isotropic phases were reached by heating the sample to about 55°C and 76°C respectively. At 3 kbar and at room temperature, the sharp signal was still present but with reduced intensity. At this pressure we did not attempt to reach the isotropic phase, because heating the Be-Cu pressure cell will weaken the material. At 5 kbar pressure the sharp signal was not present even at room temperature.

High resolution proton magnetic resonance spectrum recorded in the isotropic phase of MBBA is shown in figure 2(a). The assignment of the spectrum has already been reported in the literature (Lee *et al* 1973). The spectral width in this case was 5000 Hz. In the nematic phase three broad peaks covering a spectral range of about 41500 Hz was observed (figure 3). As the sample was cooled further, at 15°C , the broad peaks

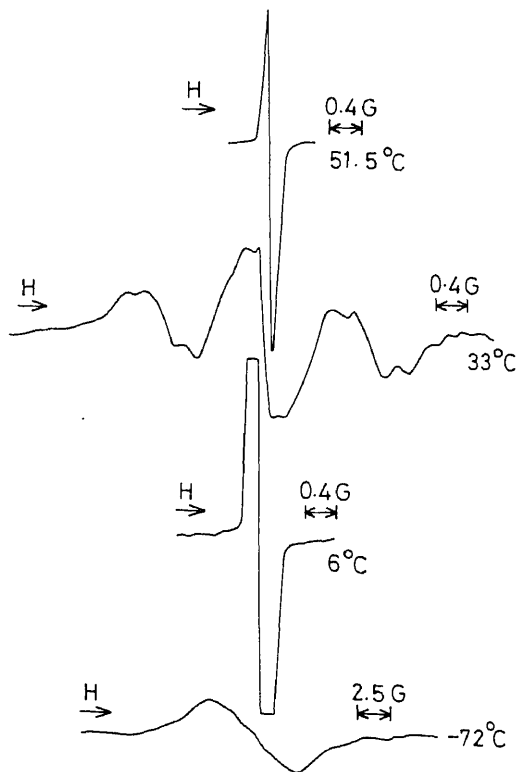


Figure 1. ^1H wideline NMR spectra of MBBA at different temperatures.

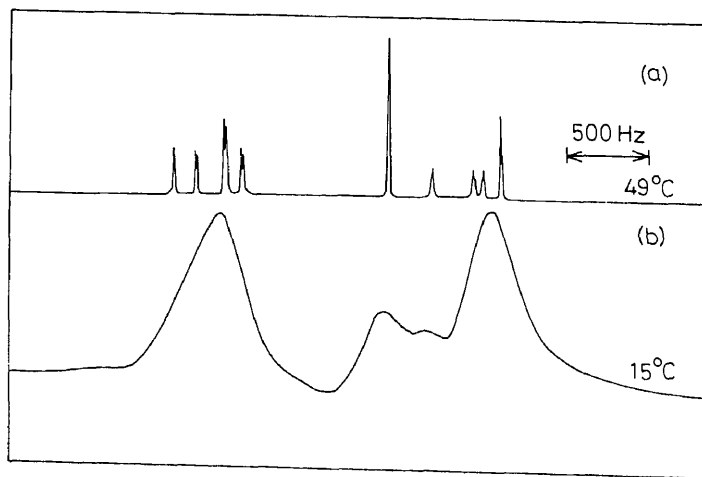


Figure 2. ^1H high resolution NMR of MBBA: (a) in the isotropic state

appeared. These lines were broader than the lines of the isotropic spectrum, but each line could be identified with different groups of lines of the isotropic spectrum as seen in figure 2(b). On further cooling these sharp lines persisted, but as the temperature was lowered they tended to become broader. At -40°C the spectrum appears to consist only of two lines because of broadening and finally around -60°C all lines completely disappear leaving a broad background signal (figure 4). As the sample is warmed up from low temperatures the spectral pattern reverses, with the exception that the solid to nematic transition is observed at 19°C . Numerical integrated intensity over the region of the sharp lines in the low temperature phase as compared to that of the nematic phase spectrum recorded under identical conditions of spectrometer settings indicates that the bulk of the material contributes to these sharp signals. There are strong indications that on cooling to the new phase from the nematic, the entire intensity resides in the narrow lines at the transition point; on cooling an increasing fraction of the molecules contribute to the broad signal. This continues till about -60°C when the entire spectrum is broad.

^2H and ^{13}C spectra were also recorded in the isotropic, nematic and phase just below the nematic phase. It was observed that in these cases also the low temperature phase spectrum consisted of narrow lines similar to the isotropic phase whereas the nematic phase spectrum consisted of much broader lines. In figure 5, ^{13}C spectra in the three phases are shown.

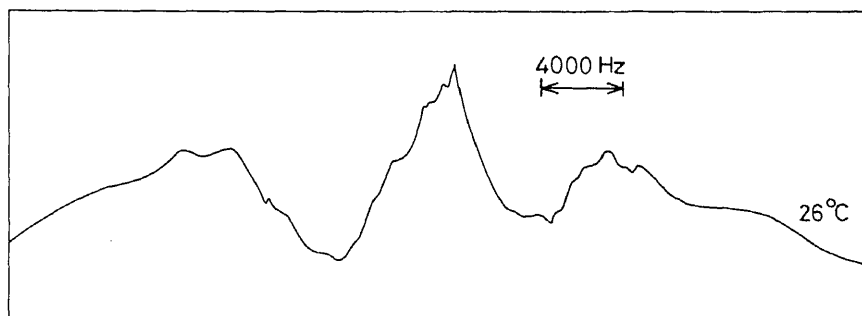
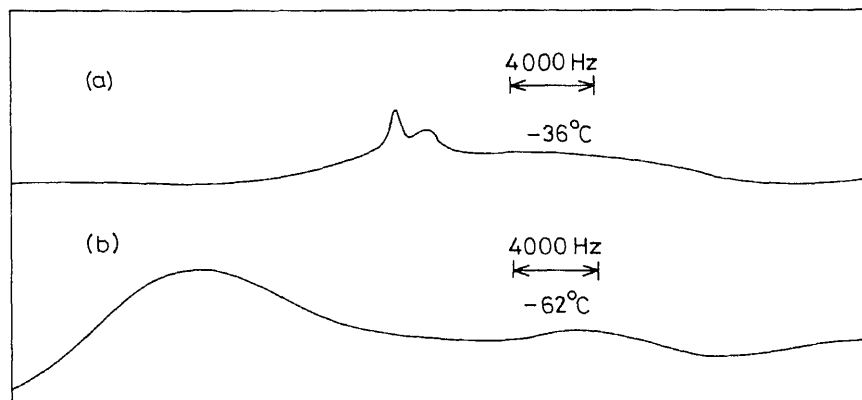


Figure 3. ^1H high resolution NMR spectrum of MBBA in the nematic phase.



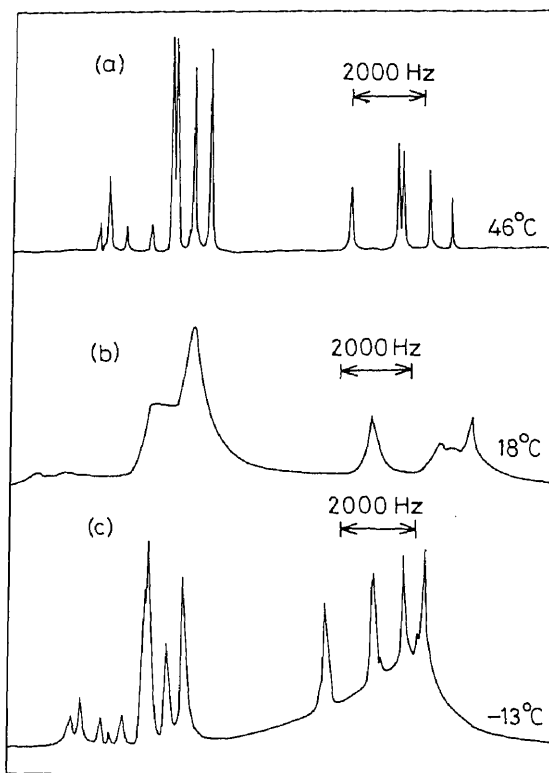


Figure 5. ^{13}C high resolution NMR spectra of MBBA at different temperatures.

We believe that this is the first report of an observation of a narrow line NMR spectrum in MBBA in the solid phase though similar observation has been made in stearic acid in its crystalline form earlier (Cyr *et al* 1967). We have taken up x-ray studies to characterise this phase of MBBA and to understand the unusual behaviour described above.

3.2 X-ray diffraction studies

A sample of MBBA was cooled to 0°C so that it is in the solid form. Powder x-ray diffractograms were taken of this sample while slowly warming it, using a Philips powder x-ray diffractometer. A typical diffractogram is shown in figure 6 which indicates the crystalline nature of the sample. The pattern is also similar to the ones obtained by Janik *et al* (1975) and Lydon and Kessler (1975).

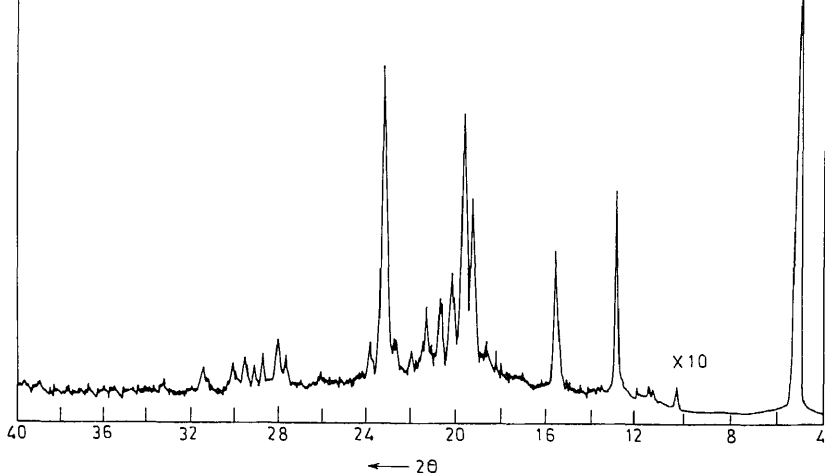


Figure 6. X-ray powder diffraction pattern of MBBA just below the nematic phase.

It must be pointed out at this stage, that anomalous behaviours have been observed in MBBA before in many other studies like x-ray diffraction (Lydon and Kessler 1975), spin-spin relaxation measurements (Ito *et al* 1981), ESR spin probe study (Stillman *et al* 1978), absorption spectra (Sciesinska *et al* 1974), IR and Raman studies (Witko and Janik 1978; Le Brumant *et al* 1976; Kirov *et al* 1980), dielectric studies (Moscicki 1976; Agarwal *et al* 1977), time-of-flight neutron spectroscopy (Bielushkin *et al* 1981) and Mossbauer study (La Price and Uhrich 1979). Most of these have been explained as due to increased mobility of various parts such as tails or the rings of the molecules of the substance in a proposed metastable state of MBBA. Further, in the majority of the studies this behaviour is reported to be monotropic, occurring while warming up of a rapidly frozen sample. We wish to emphasize the fact that what we observe is independent of the direction of change of temperature, of time and of the thermal history of the sample and whether the sample is cooled outside the magnet or within it. Therefore we conclude that what we see is a stable phase of MBBA. This conclusion is also borne out by the fact that the powder x-ray diffraction pattern just below the nematic phase as shown in figure 6 is very similar to that of 'stable' phase as observed by Janik *et al* (1975). Moreover, the isotropic liquid like very narrow (width 0.06 G) nature of the NMR lines can be accounted for only by assuming that the entire molecule is rapidly tumbling almost isotropically on the NMR time scale and not by allowing motion of just part of the molecule, either the segmental or the ring protons. Thus on the basis of the x-ray diffraction results indicative of crystalline order and the NMR results indicating rapid tumbling, we conclude that MBBA goes into a plastic crystalline state just below its nematic phase.

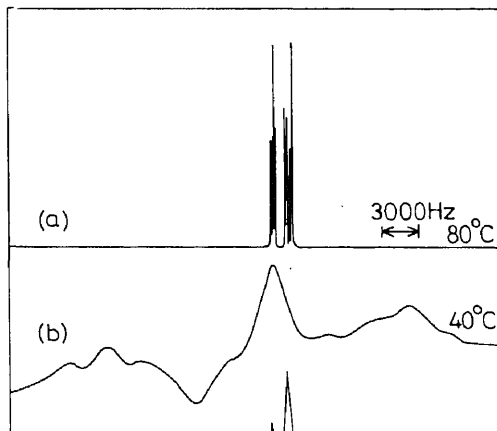
That such a transition to a plastic crystalline state is plausible can be seen in terms of Onsager's (1949) model of onset of liquid crystalline order. In this model, it is the collision of the rod-like molecules occurring at a rate faster than a critical value which maintains the orientational order of the nematogens. Thus it is conceivable that on

cooling the substance below its nematic phase into the solid phase with translational order, the collisions between the molecules cease and thus complete reorientational disorder is established where correlation time turns out to be shorter than the NMR time scale.

It must be pointed out that, high resolution NMR spectra similar to that exhibited by MBBA below its nematic phase have been observed in a few other liquid crystalline substances. Most of them however are in amphiphilic systems (Johansson and Lindman 1974)—in their so-called viscous isotropic mesophases—where individual molecules are supposed to form globular micelles which are located on the sites of a cubic lattice and 'are undergoing thermal rotatory motion at the lattice points analogous to the thermal rotatory motion of the globular molecules at the lattice points in the optically isotropic, non-amphiphilic cubic plastic crystals (Winsor 1974)'.

Finally, an earlier ESR spin probe study (Murakami and Sohma 1979) seems to indicate the presence of the plastic crystalline phase in MBBA though the phenomenon has been interpreted as melting of frozen molecular mobility on a small scale below the temperature of the bulk melting. However, as our results clearly indicate, the mobility is present over the entire sample along with translational order, establishing that what is actually observed is a plastic crystalline state. The transition temperature from nematic to this plastic crystalline state has a positive pressure coefficient, as indicated by our high pressure NMR results and from Clausius-Clapeyron equation one can conclude that the specific volume of this phase is less than that of the nematic phase.

Preliminary study of N-(*p*-ethoxybenzylidene)*p*'-*n*-butylaniline (EBBA), a substance with an additional CH₂ group attached to the methoxy side chain of MBBA, showed similar behaviour. Figure 7 shows ¹H high resolution NMR spectra of EBBA recorded at 80°C, 40°C and 20°C in the isotropic, nematic and the plastic crystalline phases respectively. It is clear that EBBA behaves in a manner similar to MBBA and it is possible that other members of the series also show similar behaviour.



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Multiple liquid crystals and NMR

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Abstract. The use of more than one liquid crystal solvents to determine molecular structure and conformation is discussed. Liquid crystals of similar and opposite signs of diamagnetic anisotropies are considered separately since they lead to different novel applications. Advantages of such experiments over those employing single solvents are pointed out with illustrative examples.

Keywords. Liquid crystals; NMR; diamagnetic anisotropy; chemical shift anisotropy; direct dipolar couplings; indirect spin-spin couplings; hetero nuclei.

1. Introduction

The use of liquid crystals as solvents in NMR experiments providing the structure and conformation of dissolved molecules is well known (Diehl and Khetrapal 1969; Emsley and Lindon 1975; Khetrapal *et al* 1975; Khetrapal and Kunwar 1977, 1983). The information for molecules with spin $\frac{1}{2}$ nuclei in diamagnetic materials is derived from the direct dipolar couplings (D_{ij} 's), the chemical shifts ($\nu_i - \nu_j$'s) and the indirect spin-spin couplings (J_{ij} 's) where i and j are the interacting nuclei. For successfully employing the technique to structural problems, therefore, precise evaluation of these parameters is essential. To derive geometrical information from dipolar couplings, the number of D_{ij} 's must not be less than the sum of the geometrical and orientational parameters in the system so as to obtain the information without having to make assumption. The use of multiple liquid crystals in NMR is a step forward in making the technique as a routine method in structural chemistry (Diehl *et al* 1980; Dombi *et al* 1980; Ambrosetti *et al* 1981; Jokissari *et al* 1981; Khetrapal *et al* 1980; Khetrapal and Kunwar 1981a, b, 1982, 1984). The experiments under different orientation conditions have been used to obtain information which would not be possible from a single experiment. Also the use of multiple liquid crystals of opposite diamagnetic anisotropies has been employed to derive the information. A few such applications are reported in the present paper. Multiple liquid crystals as media for different orientations and the use of solvents with opposite diamagnetic anisotropies are discussed separately since they both lead to different novel applications.

2. Multiple liquid crystals as media for different orientations

As pointed out in §1, the number of direct dipolar couplings obtained for a system must be larger than or equal to the number of geometrical and orientational parameters to be determined. If, however, the number of derived dipolar couplings (N) is less than the sum of the geometrical (P) and orientational (A) parameters to be derived, performing experiments under different orientation conditions *i.e.* the use of more than one liquid

$P/(N - A)$ experiments under different orientation conditions. If $P/(N - A)$ is not an integer, the minimum number is the next higher integer. It is clear that this procedure is based on the assumption that the molecular geometry is invariant from one experiment to the other. Such applications to systems such as N,N-dimethyl uracil (Khetrapal and Kunwar 1982, 1984) (μ -butatriene) hexacarbonyl diiron (Arumugam *et al* 1984) complex are reported in this section.

2.1 N,N-dimethyl uracil

The analysis of the proton NMR spectrum of N,N-dimethyl uracil (structure 1) in a single liquid crystal provides 8 HH dipolar couplings. If it is assumed that (i) axes of the methyl group rotations are along the respective N-CH₃ bonds, (ii) the methyl groups themselves are rigid, (iii) the influence of molecular vibrations are neglected, (iv) the distance between the protons 1 and 2 (r_{12}) is used as a scaling distance (2.30 Å), (v) the molecule has a plane of symmetry and (vi) the motions of the two methyl groups are not correlated, 8 geometrical parameters define the proton positions for specific modes of rotations of the methyl groups. Under such conditions, the number of order parameters for each experiment is 3. The 8 geometrical and 3 order parameters cannot be determined from a single experiment providing a total of 8 HH dipolar couplings. If, however, the experiments are performed in two different liquid crystals, the total number of 6 orientational (3 for each experiment) and 8 geometrical (assuming that the molecular geometry is invariant with solvent) can be derived from the 16 direct dipolar couplings using a least square fit procedure.

N,N-dimethyl uracil has been investigated in two liquid crystals, namely N-(*p*-methoxybenzylidene)-*p*'-*n*-butylaniline (MBBA) and *p*-*n*-butyl-*p*'-methoxysosybenzene (Merck Phase IV) (Khetrapal and Kunwar 1982, 1984). From the interpretation of the data, parameters as given in table 1 were derived. These are with respect to a right-handed Cartesian coordinate system for which the origin is at proton position 2 and the positive Y-axis lies along the line joining proton 2 to 1 with XY-plane being the molecular plane of symmetry. The derived parameters are: (i) the angle α_1 between the Y-axis and the N-CH₃ bond axis of the methyl group marked (3) in structure 1, (ii) the angle α_2 between the X-axis and the N-CH₃ bond axis of the methyl group marked (4), (iii) the (*X*, *Y*) coordinates of the centres of the equilateral triangles formed by each of the two methyl group protons—they are referred to as (*X*₃, *Y*₃) and (*X*₄, *Y*₄) for the groups (3) and (4) respectively in structure 1, (iv) (r_{HH})₃ and (r_{HH})₄, the distances within the methyl protons marked (3) and (4) respectively, and (v) two sets of order parameters denoted by S_{XX} , S_{YY} , S_{XY} and S'_{XX} , S'_{YY} and S'_{XY} for experiments in MBBA and Merck Phase IV respectively.

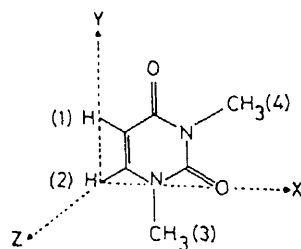


Table 1. Geometrical and order parameters in N,N-dimethyluracil

Parameter	Mode of rotation of methyl groups				X-ray values*
	E3, E4	E3, S4	E3, P4	E3, F4	
α_1 (degrees)	2.7	2.7	2.7	2.7	1.4
α_2 (degrees)	25.5	24.4	25.0	25.0	26.2
X_3 (Å)	1.88	1.82	1.85	1.85	1.95
Y_3 (Å)	-1.85	-1.83	-1.84	-1.84	-1.95
X_4 (Å)	4.78	4.84	4.81	4.81	4.76
Y_4 (Å)	2.50	2.44	2.47	2.47	2.48
$(r_{HH})_3$ (Å)	1.77	1.77	1.77	1.77	
$(r_{HH})_4$ (Å)	1.82	1.82	1.82	1.82	
S_{XX}	0.0014	-0.0008	0.0003	0.0003	
S_{YY}	0.1287	0.1287	0.1287	0.1287	
S_{XY}	0.0143	0.0199	0.0171	0.0171	
S'_{XX}	0.0093	0.0065	0.0078	0.0078	
S'_{YY}	0.1885	0.1885	0.1885	0.1885	
S'_{XY}	0.0298	0.0337	0.0337	0.0337	
RMS error (Hz)	0.08	0.10	0.09	0.09	

* Based on an average value of the methyl C-H distance and the tetrahedral value for the methyl HCH bond angles.

The above parameters were derived for each of the following modes of rotation of the methyl group(s). For the methyl group (3), (i) a free rotation (designated as F3) about the N-C bond, (ii) three energetically equivalent conformers each with a C-H bond of the methyl group pointing towards or away from the adjacent C=O group (denoted as E3 or S3 respectively), and (iii) three equivalent conformers each with a C-H bond of the methyl group perpendicular to the molecular plane of symmetry (referred to as P3) were considered. Similar possibilities were also considered for the methyl group (4) and are designated as F4, E4, S4 and P4 respectively. In this case, E4 or S4 means that one C-H bond of the methyl group (4) points towards or away from the carbonyl bond adjacent to the methyl group (3). All the combinations of the various possibilities were considered and the root-mean-square (r.m.s.) errors between the observed and the best fit calculated dipolar couplings were determined. It was observed that the r.m.s. error is larger by about an order of magnitude for all the P3 possibilities and hence they are considered less favourable. It is thus concluded that the conformation with a C-H bond of the methyl group (3) being orthogonal to the ring plane is not favoured. Table 1, therefore, does not include such possibilities. Similarly for the S3-possibilities, the r.m.s. error was nearly twice as large as for some other modes of methyl group rotations reported in table 1. Furthermore, for such cases the geometrical parameters are in complete disagreement with those obtained from x-ray data reproduced in table 1 for ready comparison. Deviations upto 0.4 Å were observed in some of the derived parameters in such cases. Hence, such conformers are also considered less favoured and the results have not been included in table 1. The F3 possibilities provided r.m.s. error comparable to that for the possibilities reported in table 1 but the derived geometrical data were in complete disagreement with x-ray crystallographic data. Consequently, the

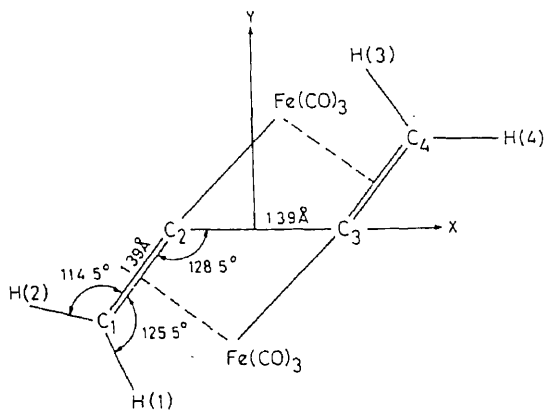
(0.08–0.10 Hz) for the E3 possibilities irrespective of the mode of rotation of the methyl group (4).

The results, therefore, indicate that the preferred conformation of N,N-dimethyl uracil is the one where one C–H bond of the methyl group (3) is the ring plane and points towards the adjacent C=O group. The results are not very sensitive to the mode of rotation of the methyl group (4). The results can be interpreted in terms of the bond polarization hypothesis (Khetrpal and Becker 1981). The C–H and the C=O bonds have opposite polarizations ($C^{\delta-} - H^{\delta+}$ and $C^{\delta+} - O^{\delta-}$) and due to electrostatic attraction, the conformer with a C–H bond of the methyl group (3) pointing towards the adjacent C=O group is preferred. On the other hand for the $CH_3(4)$ group, the presence of C=O groups on either side at about equal distances makes it hard for either the E4 or S4 conformer to be preferred. The results, therefore, are not very sensitive to the mode of rotation of $CH_3(4)$.

The geometrical data derived from NMR and x-ray studies are in reasonable agreement with each other indicating thereby that the structure does not change in going from the liquid state to the solid.

2.2 Conformation of (μ -butatriene) hexa carbonyl diiron complex:

The title compound (structure 2) provides 4 proton-proton dipolar couplings from the analysis of the spectrum in a single solvent. Since 3 of the dipolar couplings are used up for the determination of molecular order, only one item of geometrical information can be derived from the study in a single solvent. However, a study in 3 different liquid crystals permits the evaluation of the 9 order parameters (3 corresponding to each experiment) and the conformational angles θ and ϕ between the two CH_2 planes and the dihedral angle between the four carbons of the (μ -butatriene) moiety, respectively under the assumption of the reasonable bond lengths and the bond angles. A study in the three solvents, namely (i) N-(*p*'-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA), (ii) Merck Phase IV and (iii) ZLI-1167 (a ternary eutectic mixture of propyl-, pentyl- and heptyl bicyclohexyl carbonitrile) has been undertaken (Arumugam *et al* 1984) and the values of the angles θ and ϕ determined as 44° and 46° respectively.

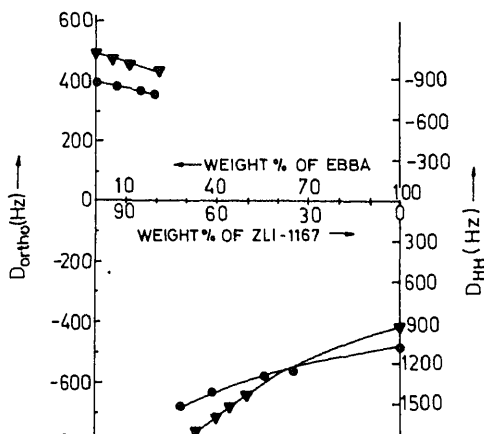


3. Multiple liquid crystals of opposite diamagnetic anisotropies

Khetrapal and Kunwar (1981) noticed that a mixture of liquid crystals with opposite diamagnetic anisotropies leads to novel application of NMR. The D_{ij} values change gradually with relative concentrations of the two solvents until at a critical concentration and temperature, they jump abruptly to twice or half with opposite signs depending upon the direction of approach of the critical point. A typical behaviour for acetonitrile and the ortho protons of benzene is shown in figure 1. A close examination of the results in the vicinity of the critical point reveals the coexistence of two types of spectra at a particular temperature with dipolar couplings in one being twice with opposite sign to those in the other as shown in figure 2. They correspond to two types of orientations of the liquid crystal optic axis, one being preferentially parallel and the other perpendicular to the magnetic field. Though the behaviour is theoretically well understood (Sinha *et al* 1983a, b, c), the question whether the two spectra near the critical point arise from certain inhomogeneities (temperature, concentration) in the sample or whether there is a "true" coexistence of the two phases, is still open. However, the experiments lead to the following novel applications: (i) determination of chemical shift anisotropy ($\Delta\sigma$) without the use of a reference or change of experimental conditions; (ii) separate determination of the indirect spin-spin and direct dipolar couplings between heteronuclei; (iii) determination of diamagnetic anisotropy of liquid crystals; (iv) precise determination of spectral parameters; and (v) determination of molecular structure with minimal distortions. These are discussed individually with illustrative examples in the following sections:

3.1 Determination of ($\Delta\sigma$) without the use of a reference or change of experimental conditions

The use of NMR spectroscopy of oriented molecules for the determination of chemical shift anisotropy is well known. It involves determination of the chemical shift difference



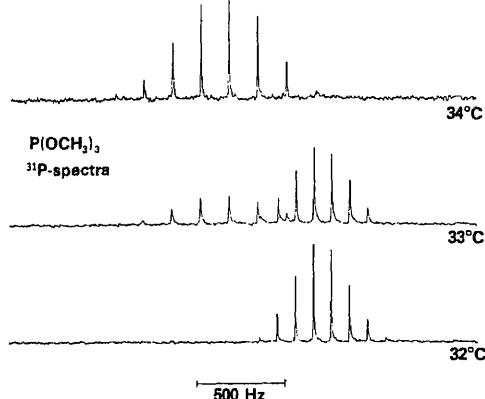


Figure 2. ^{31}P NMR spectra of trimethyl phosphite oriented in a 0.3:1 (by weight) mixture of EBBA:ZLI-1167. At 33°C, the two spectra corresponding to those at 32 and 34°C coexist.

between isotropic and anisotropic media and the order parameter. The use of equation (1) then, for a system with a 3-fold or higher axis of symmetry provides $\Delta\sigma$

$$\sigma_a = \sigma_i + \frac{2}{3} \cdot \Delta\sigma \cdot S_{C_3}, \quad (1)$$

where σ_a and σ_i are the chemical shifts in the nematic and the isotropic phases and S_{C_3} is the order parameter of the symmetry axis. In actual practice, however, the real problem lies in the precise determination of the shift difference ($\sigma_a - \sigma_i$) due to different solvent effects arising from change of experimental conditions and the need of an internal or external reference.

On the other hand, the use of mixed liquid crystals of opposite diamagnetic anisotropies near the critical point where the "coexistence" of two spectra is observed, permits evaluation of the chemical shift anisotropy without using a reference or changing the experimental conditions. Equation (2) is valid for a molecule with 3-fold or higher axis of symmetry

$$\Delta\sigma = (\sigma_{\parallel} - \sigma_{\perp}) / (S_{C_3}), \quad (2)$$

where $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the chemical shifts for the orientations corresponding to $\Delta\chi > 0$ and $\Delta\chi < 0$ respectively and (S_{C_3}) is the order parameter of the symmetry axis for the orientation with $\Delta\chi > 0$.

The method has been used to obtain proton as well as carbon-13 chemical shift anisotropies (Khetrpal and Kunwar 1981b; Raghothama 1984). An interesting comparison of the values of the chemical shift anisotropies determined using various methods has been made (Diehl *et al* 1982a). It has been concluded that this method proposed by Khetrpal and Kunwar (1981) and named as NEMIX method (Diehl *et al* 1982a) provides most satisfactory results. Although the NEMIX method provides satisfactory results, the "local effects" on the chemical shifts are present even for this method and they may at times lead to unrealistic results (Khetrpal *et al* 1984a,b) if such effects are not taken into account. Theoretical calculations to estimate such effects

It is well known that the nuclear spin Hamiltonian for oriented systems contains the sum $(J_{AX} + 2D_{AX})$ when A and X are heteronuclei. Consequently, individual determination of the direct dipolar and the indirect spin-spin couplings is not possible in such cases. In order to obtain precise value of D_{AX} for accurate evaluation of molecular geometry, J_{AX} must be known. Since J_{AX} may be temperature and solvent-dependent specially when heavy nuclei are involved, it may be appropriate to obtain its value in the nematic phase itself without changing experimental conditions. This can be achieved conveniently from the coexistence of the two spectra near the critical point in mixed liquid crystals of opposite diamagnetic anisotropies. The quantities $(J_{AX} + 2D_{AX})$ and $(J_{AX} - D_{AX})$ (where D_{AX} is the dipolar coupling for the orientation corresponding to $\Delta\chi > 0$; the value for $\Delta\chi < 0$ near the critical point is $-\frac{1}{2}D_{AX}$) provide J_{AX} and D_{AX} individually.

The first demonstration of this application was made for acetonitrile (Khetrapal and Kunwar 1981) where the indirect and the direct couplings between protons and ^{13}C and ^{15}N in the natural abundance have been determined. Subsequently, the values for phenyl selenyl chloride and bromide (Suryaprakash *et al* 1983a,b), trimethyl phosphate (Khetrapal *et al* 1984) and trimethyl phosphite (Subburam 1984) have been obtained and the molecular geometries determined.

3.3 Determination of diamagnetic susceptibility anisotropy of liquid crystals

A direct consequence of the experiments in mixed liquid crystals of opposite diamagnetic anisotropies is that the macroscopic diamagnetic anisotropy of the system at the critical point vanishes *i.e.*

$$p(\Delta\chi)_{\parallel} + (1-p)(\Delta\chi)_{\perp} = 0, \quad (3)$$

where p is the mole-fraction of the solvent with $\Delta\chi > 0$ and $(\Delta\chi)_{\parallel}$ and $(\Delta\chi)_{\perp}$ are the diamagnetic susceptibility anisotropies of the components with $\Delta\chi > 0$ and $\Delta\chi < 0$ respectively. Both $(\Delta\chi)_{\parallel}$ and $(\Delta\chi)_{\perp}$ are related to molar susceptibility anisotropy $(\Delta\chi_a)$ by the relation $\Delta\chi = S_{\text{LC}} \cdot \Delta\chi_a$ where S_{LC} is the order parameter of the liquid crystal. This method has been proposed and used by Diehl and Jokisaari (1982) using a solute as the probe molecule. Relative diamagnetic anisotropies of a number of liquid crystals have been thus obtained.

3.4 Precise determination of spectral parameters

When the number of observed transitions in a nuclear spin system is not very large compared to the number of spectral parameters to be derived, it may sometimes turn out that the derived spectral parameters suffer from large uncertainties. Such a situation was actually encountered for the proton NMR spectra of the type AB_2 in 2,6-dichlorophenol (Lakshminarayana *et al* 1985). The system was studied in a mixture of EBBA and ZLI-1167 and the spectra were analysed above and below the critical point. Values of the indirect coupling J_{AB} determined from the two spectra were -7.3 and $+10.1$ Hz. On the other hand, near the critical point where the two orientations "coexist", values of the dipolar couplings are related by a factor -2 . Using this condition and analysing the spectra near critical point provides $J_{AB} = 8.3$ Hz which is identical to the value determined from the analysis of the spectrum in an isotropic medium.

There has recently been a great interest in the study of solvent effects on the structure of molecules derived from NMR studies of oriented systems. A systematic study of benzene in various liquid crystals has been undertaken and it has been concluded that the distortions are minimal in liquid crystals such as ZLI-1167 with no aromatic rings (Diehl *et al* 1979). On the other hand, in thiophene largest distortions have been observed in the solvent ZLI-1167 (Diehl *et al* 1983). Similarly in N-methyl pyrrole, the distortions are less in the solvent ZLI-1167 (Suryaprakash *et al* 1984) whereas they are quite large in the same solvent for benzo(b)selenophene (Suryaprakash *et al* 1985). A study of acetonitrile in various liquid crystals has been undertaken and the distortions in molecular structure have been correlated to the diamagnetic anisotropy of the solvent (Diehl *et al* 1982b). Since the macroscopic diamagnetic susceptibility anisotropy vanishes at the critical point, it is concluded that the distortions are minimal when the studies are performed near the critical point. It has actually been demonstrated to be so in systems such as methane (Jokisaari and Hiltunen 1983) and N-methyl pyrrole also.

It is, therefore, concluded that the NMR studies of molecular structure using liquid crystal solvents should be performed around the critical point in mixed liquid crystals of opposite diamagnetic anisotropies in order to derive the molecular geometry with minimal distortions.

4. Conclusions

It is demonstrated that the NMR studies of molecules oriented in more than one solvent provide more information on molecular structure than single liquid crystals. When the multiple liquid crystals are of opposite diamagnetic anisotropies, they lead to novel applications of NMR. Furthermore, mixed liquid crystals of opposite diamagnetic anisotropies provide media with minimal distortions in molecular structure.

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NMR imaging: Mathematical modelling and spectrometer design considerations

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Abstract. The mathematical modelling of 'NMR imaging' is presented from the electrical system design viewpoint. The response, namely, the magnetisation $M_{xy}(t)$, is linearly related to a system identification function made up of the nuclear spin density distribution $\rho(\mathbf{r})$ and the relaxation times $T_1(\mathbf{r})$ and $T_2(\mathbf{r})$, while the r.f. excitation affects the system nonlinearly and appears as an 'aperture' function in the imaging equation.

Spectrometer design considerations indicate that the resolution is limited by noise at the detection stage. In our imaging spectrometer developed for studying multiphase biospecimens, a 1 mm image resolution is feasible with a gradient of $50 \mu T cm^{-1}$, assuming a 200 Hz frequency resolution and signal averaging.

Keywords. NMR imaging; mathematical modelling; NMR imaging spectrometer; Zeugmatography.

1. Introduction

The use of nuclear magnetic resonance (NMR) as an important imaging technique originated with Lauterbur (1973) who proposed the addition of linear field gradients to the homogeneous magnetic field in order to transform the conventional (*i.e.*, zero-dimensional) NMR signals into projections which represent integrated values of the signals along lines or planes of an object. NMR imaging, or *zeugmatography* as Lauterbur originally called it, is thus already a decade old, and the initial experiments have stimulated the evolution of various modalities within the main framework of NMR.

However, with the present-day requirements of full-scale systems for use in a variety of biophysical and biomedical applications, it becomes necessary to identify, if not indeed unify, the common elements underlying the various modalities. Any meaningful comparison of several possible approaches to NMR imaging, from the electrical 'systems' viewpoint, necessitates the development of appropriate imaging equations based on a mathematical model. For the conventional NMR phenomenon, a good mathematical model is already available in the form of the well-known Bloch equations (Bloch 1946). However, the nonlinear characteristics of a 'driven' NMR system have somewhat restricted the development of simple quantitative models for describing the response, especially to arbitrary excitation pulses. This important point has been made recently in several elegant descriptions of NMR imaging (Hoult 1979; Mansfield *et al* 1979; Caprihan 1983; Hinshaw and Lent 1983).

Before discussing the mathematical model, we briefly recall the basic theory of NMR and NMR imaging, and review the presently known imaging modalities in the following

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three sections. In § 1.4, an overview is given of the essential radiofrequency (r.f.) pulse sequences and magnetic field gradients which provide the input 'excitations' to the nuclear spin system.

In § 2 we develop the mathematical model based on the 'systems' approach, and critically examine the imaging equations from several points of view. In § 3 are derived the response functions when the system is driven by basic excitations characteristic of several imaging modalities. In § 4, reception of the response signal is considered, and 'noise' and the spectrometer 'figure of merit' are discussed. Lastly, we outline the design criteria adopted in the construction of an imaging spectrometer in our chemistry laboratory for studying multiphase biosamples, and present its block schematic diagram.

1.1 Some basic theory

A nucleus with an odd mass number such as ^1H possesses the quantum mechanical property of intrinsic *spin* angular momentum. $\mathbf{I}\hbar$, the possession of both spin and charge conferring on it a magnetic dipole moment $\mu = \gamma\hbar\mathbf{I}$ (recall the classical electromagnetic analogue of a charged mass spinning in a circular orbit generating a magnetic moment). According to fundamental NMR theory (Abragam 1961), when a physical specimen containing an ensemble of such dipoles is polarised in a constant d.c. magnetic field $\mathbf{B}_0$ along, say, the z-direction of the xyz laboratory coordinate system, it develops a macroscopic magnetisation, $\mathbf{M}$, which is the vector sum of the μ 's of the individual nuclei. $\mathbf{M}$ then experiences a torque proportional to $\mathbf{M} \times \mathbf{B}_0$ at the angular rate

$$\omega = -\gamma\mathbf{B}_0 \quad (1)$$

and the differential equation governing this precessional motion is given by

$$d\mathbf{M}/dt = \gamma\mathbf{M} \times \mathbf{B}_0. \quad (2)$$

The introduction of a circularly polarised r.f. magnetic field $\mathbf{B}_1(t)$ (at the angular frequency ω) in the plane orthogonal to the z-axis tends to 'nutate' the magnetisation $\mathbf{M}$ about its instantaneous axis, and 'resonant absorption' of r.f. energy occurs. In the xyz frame, the nett magnetisation is now the resultant $\mathbf{B}_{\text{res}} = \mathbf{B}_0 + \mathbf{B}_1(t)$, and the resultant nutation frequency is $\omega_{\text{res}} = -\gamma\mathbf{B}_{\text{res}}$.

Mathematically, resonance is better handled by adopting a reference frame $x'y'z'$ which *rotates* about the z-axis at frequency ω in the same sense as the precessing nuclear magnet. The effect of $\mathbf{B}_0$ gets subsumed in this rotating frame, and we have

$$|\omega_{\text{res}}|_r = \gamma|\mathbf{B}_1|_{\text{max}}. \quad (3)$$

$(\omega_{\text{res}})_r$ is the nutation frequency in the rotating frame, and is an important variable in NMR.

If the r.f. field is left on for a duration t_p , the angle ϕ by which $\mathbf{M}$ nutates is given by

$$\phi = \gamma|\mathbf{B}_1(t)|t_p. \quad (4)$$

ϕ is termed the nutation or 'flip' angle. Remembering in our formulation that the observation plane for the magnetisation is $x'y'$, it is seen that to obtain maximum NMR signal response due to the nett transverse component $\mathbf{M}_{x'y'}$, ϕ must be 90° . The application of a $\pi/2$ - or 90° -r.f. 'pulsed' excitation achieves this. As a further important

of the $\mathbf{M}_{x'y'}$ response signal in the time domain, $s(t)$, is called the *free induction decay* (FID).

The basic mathematical model of NMR is developed from the differential equation of motion, equation (2), in the rotating frame, and includes the two important relaxation times, T_1 and T_2 . The first of these, the spin-lattice relaxation time, characterises the restoration of thermal equilibrium of the spin ensemble with the 'lattice', or return of the nett magnetisation to the z -axis in presence of $\mathbf{B}_0$. On the other hand, T_2 is characteristic of the loss of phase information amongst the spins under the influence of the 'spread' in the local dipolar field, and does not lead to restoration of thermal equilibrium of the overall spin-lattice system. Addition of these two rate factors to (2) completes the set of Bloch phenomenological equations,

$$\frac{d\mathbf{M}_{x'y'}}{dt} = \gamma \mathbf{M} \times \mathbf{B} - \frac{M_x}{T_2} \mathbf{i}_x - \frac{M_y}{T_2} \mathbf{i}_y - \frac{(M_0 - M_z)}{T_1} \mathbf{i}_z. \quad (5)$$

In (5), $\mathbf{B} = B_0 \mathbf{i}_z + B_{1x}(t) \mathbf{i}_x + B_{1y}(t) \mathbf{i}_y$ is the resultant magnetic field ($\mathbf{i}_x$, $\mathbf{i}_y$ and $\mathbf{i}_z$ being unit vectors), and B_{1x} and B_{1y} are the components of the circularly polarised r.f. magnetic field. In the terminology of electrical signal systems, the Bloch equations thus typify a 'lumped' model wherein the vector dynamical equation of the bulk nuclear magnetisation is established taking account of the damping factors due to the two spin relaxation mechanisms.

1.2 Principles of NMR imaging

The concept of 'imaging' an object using NMR follows logically from the background in the previous section. The resonance equation (1), implies that the superposition of a spatially varying magnetic field $\mathbf{B}(\mathbf{r})$ over $\mathbf{B}_0$ amounts to a spatial variation of the resonance frequency

$$\omega(\mathbf{r}) = -\gamma(\mathbf{B}_0 + \mathbf{B}(\mathbf{r})). \quad (6)$$

The variation $\omega(\mathbf{r})$ is linear if $\mathbf{B}(\mathbf{r})$ varies linearly over $\mathbf{r}$. $\mathbf{B}(\mathbf{r})$ may be written as

$$\mathbf{B}(\mathbf{r}) = -\mathbf{G}(\mathbf{r}) \cdot \mathbf{r}, \quad (7)$$

where $\mathbf{G}(\mathbf{r})$ is the magnetic field gradient. In the simple case of a field gradient in the x -direction,

$$\omega(x) = -\gamma(\mathbf{B}_0 + \mathbf{G}_x \cdot x), \quad (8)$$

where the gradient is imposed over the main magnetic field.

Alternatively, (8) implies a mapping between the spatial coordinate x and the frequency $\omega(x)$. The primary response in NMR imaging is the distribution of the *density* of nuclear spins, say, the protons. In a proton-containing object, this amounts to an image-formation, with the spin density distribution denoting the intensity of the image. One should also note that the resolution is determined by the magnitude of the magnetic field gradient $G_x(x)$ rather than the wavelength of excitation.

1.3 A review of current imaging modalities

NMR imaging is marked by a variety of ways of obtaining a map of the nuclear density distribution in an object. The reason for this is the basic imaging equation itself, as will

field gradient, in conjunction with the FM extension, represents a response to a small region in space. Therefore, the various modalities represent the ways in which the sample responses may be grouped together for spatial encoding.

Broadly, imaging modalities may be classified as being 'reconstructive' or 'non-reconstructive'. The former technique is an adaptation of the principles of image generation in x-ray computerised tomography (Hounsfield *et al* 1973; Scudder 1978), and involves reconstruction of the image in its entirety from integral projections. The procedure for extracting the image from a signal received in the time domain, $s(t)$, may be understood from

$$s(t) = \int_x \rho(x) \exp(i\gamma G_x x t) dx, \quad (9)$$

which indicates a Fourier transformation between $\rho(x)$ and $s(t)$, where

$$\rho(x) = \int_y \int_z \rho(xyz) dy dz. \quad (10)$$

Thus $s(t)$ contains the *plane integral*, equation (9). The image is then obtained by invoking a suitable algorithm for 'back-projecting' (see figure 1) to reconstruct a 3-D or 2-D image from projections. This necessitates scanning the object space, which is also the $K_x - K_y$ phase space ($K_x = \gamma G_x \cdot x$, $K_y = \gamma G_y \cdot y$; see the phase factor in (9)) probed by the magnetic field gradients (Locher 1984).

Modalities in which an image reconstruction scheme is not involved are classified as non-reconstructive. Successful techniques that fall under this classification are (i) the point and line-scan imaging (Mansfield and Maudsley 1976; Maudsley 1980), (ii) direct Fourier transform (DFT) imaging (Kumar *et al* 1975), and (iii) sensitive-point imaging

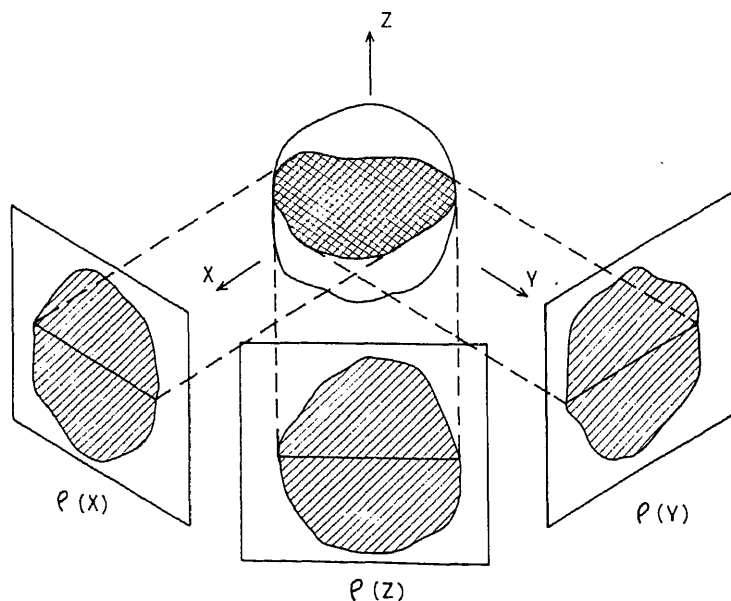


Figure 1. A pictorial representation of 'reconstruction', where the plane integrals are back-projected to obtain the image.

'exciting', or bringing into resonance, a particular region of the sample (a line or a point) at a time, and recording the response. The process is repeated to map the whole sample region. A detailed discussion of this modality has been published recently (Cho *et al* 1982).

DFT imaging involves line-scanning the phase plane, so that spatial information is encoded into the *phase* behaviour of the spin magnetisation. The data is processed either in 2-D or 3-D format depending on the mode of scanning which is achieved by switching the x , y and z -gradients, and is then subject to a direct Fourier transform for image formation. Often this is the preferred modality of imaging in biomedical contexts.

The third modality, sensitive-point imaging, uses time-dependent magnetic field gradients for recovering spatially resolved signals. The field gradient is carefully set up to be time-dependent everywhere except within a small region of interest, the 'sensitive point'. Because the NMR signals from the regions of time-dependent field are frequency-modulated, only the sensitive point gives a nonvanishing signal after low-pass filtering. Then, by controlled variations of the relative currents in the coils supplying the alternating gradients, the sensitive 'spot' may be shifted in much the same way as the scanning spot in tv, to build up a complete scan (or 'raster') in, say, the xz plane, thus producing an image 'slice' through the object. A stack of such slices provides the complete 3-D image. Data acquisition here is slow, and affects imaging time—an important factor in biomedical applications.

1.4 Modes of excitation of the system being imaged

1.4a *R.f. pulses*: The B_1 -field may be tailored to stimulate either the whole sample or specific regions. Consequently, there are (a) 90° and 180° broadband pulses and (b) 90° and 180° narrow-band pulses. The power spectra of the broadband pulses are designed to excite the whole sample in the presence of strong field gradients. The power requirements on these pulses are, however, large; they are therefore sparingly used in imaging experiments. In most imaging techniques, 90° pulses initiate a sequence and may be applied before imposing the field gradients, thereby obviating the necessity for broadband stimulus.

The narrow-band 90° and 180° r.f. pulse excitations are used to stimulate selectively a region of the sample, and are important in non-reconstructive modalities, *e.g.* to effect slice selections in 2-D DFT imaging.

1.4b *Magnetic field gradients*: The two types of field gradients used in imaging are (a) read-out gradient and (b) pulsed gradient. The first is a constant gradient applied in a particular direction, say the x -axis, for a duration t much longer than the spin-dephasing time, $t \gg 1/\gamma G_x L$ (where L is the spatial extent of the sample over which FID signals are collected). The purpose is to effect the read-out of the response, and is used in line-scan and DFT imaging.

The term 'pulsed gradient' refers to the case where the duration of the gradient is shorter than the spin dephasing time so that the transverse magnetisation remains in phase while being modified marginally by the pulse.

2. Mathematical model of NMR imaging: A 'systems' approach

The characteristics of NMR imaging for purposes of 'system identification' depend on the three most important parameters, $\rho(\mathbf{r})$, $T_1(\mathbf{r})$ and $T_2(\mathbf{r})$. Mapping the spatial information onto the frequency spectrum is achieved by applying $\mathbf{G}(\mathbf{r})$. Consequently, considering the total NMR system as a black box, the inputs are $\mathbf{G}(\mathbf{r})$ and the r.f. excitation, $\mathbf{B}_1(t)$, while the output is the FID, $s(t)$. The main magnetic field B_0 defines the operating frequency of the experiment and is not presented as an input, since some form of demodulation or frequency translation is inherently assumed. Figure 2 describes schematically our 'systems' approach. The following remarks may be made at the outset before commencing our analysis: (a) the relationship between the input and output is involved, due to the nonlinearity of the Bloch equations; (b) the system is 'multi-input' and 'single-output' in nature, a fact to be borne out by the model to be developed, and (c) any linearity in the system, if present, is not obvious on a cursory examination.

In the rotating reference frame $x'y'z'$, we define (a) the residual field due to the field gradient at location $\mathbf{r}$ as $\Delta B(\mathbf{r})$, and (b) the frequency of $\mathbf{B}_1(t)$ as ω_0 . The Bloch equation in the rotating frame is then modified to

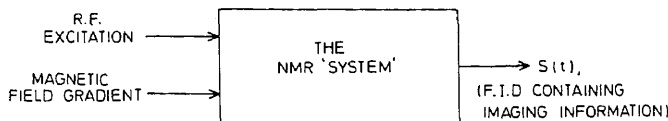
$$(d\mathbf{M}/dt)_{\text{rot}} = (\mathbf{M})_{\text{rot}} \times \mathbf{B}^* - \frac{M_{x'}}{T_2} \mathbf{i}_{x'} - \frac{M_{y'}}{T_2} \mathbf{i}_{y'} - \frac{(M_{z'} - M_0)}{T_1} \mathbf{i}_{z'}, \quad (11)$$

where $\mathbf{B}^* = \Delta B(\mathbf{r})\mathbf{i}_{z'} + B_1(t)\mathbf{i}_{x'} + 0 \cdot \mathbf{i}_{y'}$ (obtained by choosing the x-axis along the $B_1(t)$ phasor) and, by definition, $(\mathbf{M})_{\text{rot}} = M_{x'}\mathbf{i}_{x'} + M_{y'}\mathbf{i}_{y'} + M_{z'}\mathbf{i}_{z'}$, all components being functions of t and $\mathbf{r}$ (with respect to the laboratory frame). Since orthogonal components of the magnetisation in the transverse plane of the rotating coordinates have a quadrature phase relationship in the laboratory frame, we define M as $M = M_{x'} - iM_{y'}$ and simplify the Bloch equations as

$$\begin{aligned} \frac{dM}{dt} + \left(\frac{1}{T_2} - i\gamma\Delta B(\mathbf{r}) \right) M &= -i\gamma\mathbf{B}_1(t)M_{z'}, \\ \frac{dM_{z'}}{dt} &= \gamma\mathbf{B}_1(t) \text{Im}(M) - \frac{M_{z'} - M_0}{T_1}. \end{aligned} \quad (12)$$

The term corresponding to T_1 may be neglected for all $t < T_1$. We have written the Bloch equations for a spatial location $\mathbf{r}$ in the sample, so that $M_{x'}$, $M_{y'}$, $M_{z'}$, T_1 and T_2 are functions of $\mathbf{r}$ (the location in the laboratory frame).

The NMR response is observed in the $x'y'$ plane, and so $M(t)$ is the variable of interest. The vector dynamical equations are then coupled, and nonlinearity is imposed through the time-varying r.f. field envelope $\mathbf{B}_1(t)$ which appears as a coefficient in the differential equations above. When $\mathbf{B}_1(t) = 0$, a situation that prevails at the end of the r.f. pulse, the evaluation of M is governed by linear differential equations. Therefore the FID signal



may be regarded as the output of a linear system whose initial conditions are related to $B_1(t)$ in a nonlinear fashion. This important point emerges more clearly from our geometrical arguments that follow.

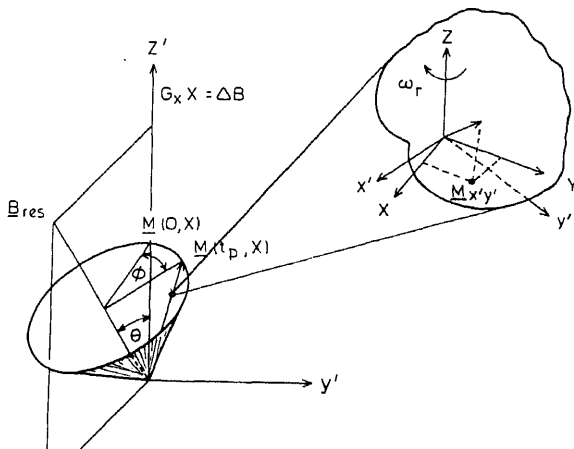
2.1 The basic NMR imaging equation (from geometrical arguments in the rotating reference frame)

We shall now construct the imaging equation by considering purely geometrical aspects of the precessing magnetisation. We assume that the resonance condition, equation (1), holds for the pulse duration t_p , and that $t_p \ll T_1, T_2$. We further assume that the modulating r.f. pulse envelope is rectangular, i.e., $B_1(t) = B_1$, a constant, for $0 \leq t \leq t_p$. For simplicity we consider a single gradient $\mathbf{G}_x$ along the x -direction. The symbols to be used in our treatment are (i) $M_0(x)$, the equilibrium magnetisation in the interval Δx around x ; (ii) $\rho(x)$, the one-dimensional spin density distribution, equation (10), and (iii) A , the cross-sectional area of the sample.

Figure 3 illustrates the precession of the resultant magnetisation in the $x'y'z'$ frame. The precession cone, indicated by broken lines in the figure, has its axis tilted by θ with respect to the z' axis. The cone degenerates to a circle at $x = 0$ where $\Delta \mathbf{B}(x) = 0$. The associated equations are $|\mathbf{B}_{\text{res}}| = [(\Delta \mathbf{B})^2 + \mathbf{B}_1^2]^{1/2}$, $\tan \theta = B_1/\Delta B = B_1/G_x x$ where θ is the 'tilt' angle, and $\phi = \gamma |\mathbf{B}_{\text{res}}| t_p$ is the 'flip' angle.

At time t_p , the magnetisation has the orientation determined by ϕ , θ and $M_0(x)$. For a general initial condition $\phi_1 = \phi|_{t=0} (\neq 0)$, the projections of the magnetisation along the x' , y' and z' axes are

$$\begin{aligned} M_{x'} &= M_0(x) \{ \cos \psi \sin \theta - \sin \psi \cos(\phi_1 + \phi_r) \cos \theta \}, \\ M_{y'} &= M_0(x) \{ \sin \psi \sin(\phi_1 + \phi_r) \}, \\ M_{z'} &= M_0(x) \{ \sin \psi \cos(\phi_1 + \phi_r) \sin \theta + \cos \psi \cos \theta \}, \end{aligned} \quad (13)$$



ϕ_r is the instantaneous flip angle.

At the end of the r.f. pulse, the magnetisation precesses freely about the z -axis at a rate $\Delta\omega = \gamma\Delta B_x$, and therefore,

$$M_{x'}(x) = M_0(x)F_{x'}(x),$$

and

$$M_{y'}(x) = M_0(x)F_{y'}(x),$$

where $F_{x'}$ and $F_{y'}$ are the projections, or *aperture functions*, of $M_0(x)$ at time t_p . Writing $M(x)$ as

$$M(x) = M_{x'}(x) - iM_{y'}(x),$$

or

$$F(x) = F_{x'}(x) - iF_{y'}(x) = \frac{1}{M_0(x)}(M_{x'} - iM_{y'}), \quad (14)$$

the magnetisation $M_0(x)$ in turn may be expressed as

$$M_0(x) = K\rho(x),$$

where K is a constant of proportionality relating nuclear spin density to magnetisation. At the end of the pulse duration, $M_{x'y'}(x) = KF_{x'y'}(x)\rho(x)$, where the subscripts indicate that the phasors M and F are in the $x'y'$ plane, and are implicitly assumed henceforth. The future evolution of the magnetisation is determined by the field gradient $\Delta B = G_x x$. Thus,

$$M(t) = KF(x)\rho(x)\exp(i\gamma G_x x t).$$

The overall response from the entire sample aggregate is the magnetisation $m(t)$, where

$$m(t) = KA \int_x F(x)\rho(x)\exp(i\gamma G_x x t) dx. \quad (15)$$

So far in our derivation the effect of T_1 and T_2 has been neglected on the assumption that $t_p \ll T_1, T_2$ which is not valid for the long-term evolution of the magnetisation. Their first order effect (when $1/G_x L \ll T_2$) is a multiplicative term, $\exp(-t/T_2)f(T_1)$, and hence

$$m(t) = KA \left[\int_x F(x)\rho(x)\exp(i\gamma G_x x t) dx \right] \exp(-t/T_2)f(T_1). \quad (16)$$

This expression, cast in the form of a Fourier transformation, is the basic imaging equation. The term $F(x)$ is the aperture function modifying the effect of $\rho(x)$.

For the most common case of a rectangular pulse, applied to bring about a 90° flip of the magnetisation, $\phi_1 = 0$ and $\psi = \theta$ in (13), combining these with (14), one gets

$$F(x) = \sin \theta \cos \theta (1 - \cos \phi) - i \sin \theta \sin \phi, \quad (17)$$

while the expression is fairly complex in the case of arbitrary pulse excitations. The imaging equation, (16), leads to the following important observations:

- (i) the response $m(t)$ is linearly related to the system identification parameter, $\rho(x)$;
- (ii) the aperture function, $F(x)$, is nonlinearly related to the r.f. excitation, $B_1(t)$.

Equation (16) assumes an even more general form when the relaxation effects are spatially-dependent, and are therefore no longer exponential. The resultant transverse magnetisation (i.e., signal) in 3-D would then be represented as

$$m(t) = K \int_V F(\mathbf{r}) \rho(\mathbf{r}) L(\mathbf{r}, t) \exp(i\gamma[\mathbf{G}(\mathbf{r}) \cdot \mathbf{r}]t) dV. \quad (18)$$

Our master equation, (18), may be interpreted in terms of *transfer functions*, where $\rho(\mathbf{r})$ and $L(\mathbf{r}, t)$ define the system parameters to be identified, and $m(t)$ may be treated as the impulse response of the transfer function $F(\mathbf{r})\rho(\mathbf{r})L(\mathbf{r}, t)$ as shown in figure 4.

2.2 Arbitrary excitations: Use of perturbation techniques

For the usual case of rectangular r.f. pulses, and for $\mathbf{B}_1 \cong G_x x$, it is easily seen from (17) that the components of $F(x)$ in the observation plane are

$$F_x(x) = \frac{B_1 |G_x x|}{[B_1^2 + (G_x x)^2]^{1/2}} \{1 - \cos(\gamma[B_1^2 + (G_x x)^2]^{1/2} t_p)\},$$

and

$$F_y(x) = B_1 \gamma t_p \operatorname{sinc}(\gamma[B_1^2 + (G_x x)^2]^{1/2} t_p). \quad (19)$$

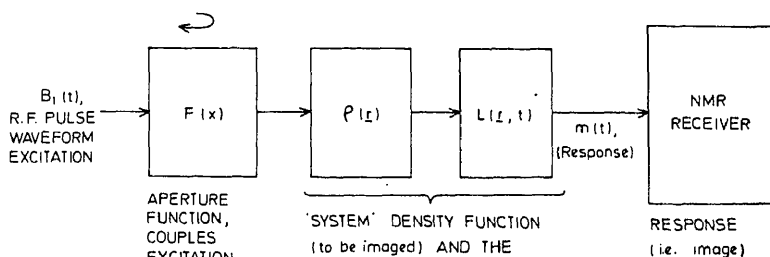
The solution for arbitrary excitations, however, may be obtained numerically using a piecewise rectangular approximation in the rotating frame (Caprihan 1983). Indeed, it may be shown that Gaussian, sinc and triangular modulations are 'good', if not optimum, r.f. excitations. More generally, the application of perturbation expansion techniques (Hoult 1979; Raghunathan 1981) helps one either to determine $F(x)$ or to design the $B_1(t)$ pulse to obtain a specific form for $F(x)$. This procedure may be important in selective excitations where image resolution is mainly determined by the aperture function.

In the perturbation approach, the magnetisations $M(t)$ and $M_z(t)$ are written as a series of terms of order $\gamma B_1(t)$,

$$M(t) = M^{(0)} + M^{(1)} + \dots,$$

$$M_z(t) = M_z^{(0)} + M_z^{(1)} + \dots \quad (20)$$

For the general perturbation terms $M^{(n)}$ and $M_z^{(n)}$, the Bloch equations yield (Hoult 1979)



with the initial conditions $M^{(0)} = 0$ and $M_z^{(0)} = M_0(\mathbf{r})$, while the effect of neglected.

The above equations are recursive; the equations for the first few orders lead to results,

$$M_z^{(1)} = 0, M_z^{(2)} = 0, M_z^{(2)} = \int_{-\infty}^t \gamma B_1(t) \operatorname{Im} M^{(1)} dt.$$

The following interesting result transpires from the above. At $\mathbf{r}_0$, where $\Delta B(\mathbf{r}_0) = 0$, the magnetisation vector precesses about $B_1(t)$ or the x' axis. The flip angle for this case is given by $\phi = \gamma \int B_1(t) dt$. Since the effect of the perturbation term is in the product $B_1 |t_p$ (or in B_1 for a given t_p), the flip angle may be treated as an indicator of the nonlinearity.

Some other important observations resulting from the perturbation solutions of the Bloch equation are: (i) the equation governing $M^{(1)}$ is linear, and predominant for small flip angles, and operation in the linear region has the advantage of easy system design as $F(x) = \mathcal{F}(B_1(t))$, $\mathcal{F}$ denoting Fourier transformation; (ii) in the presence of a strong, linear field gradient, the magnetisation $M^{(1)}$ at time t_p is negligible, and may be observed only with a 'spin echo' pulse sequence (Hahn 1950; Carr and Purcell 1946); this is due, of course, to quick spin-dephasing by the gradients; (iii) the r.f. excitation should not possess sharp edges, as this increases side-lobe power in the perturbation response which reduces selectivity.

The Bloch equations and our geometrical arguments presented in the previous section are related by the fact that, while the former reflect magnetisation dynamics in the $x'y'z'$ frame, we treat the problem in a frame somewhat tilted with respect to the $x'y'z'$ axis system. The vector $\mathbf{B}_{\text{res}}$ (figure 3) is along one of the axes of this tilted frame. It may be derived from our geometrical formulation that, for $\Delta B < (B_1)_{\text{max}}$, $M_z^{(n)} = M_0(x) \cos^n \phi - i M_0(x) \sin \phi$. The perturbation term $M^{(n)}$ of (21) corresponding to this situation takes the form (Raghunathan 1981)

$$M^{(n)} = -i(\phi^n/n!)(-1)^{(n-1)/2} M_0(x) \text{ for } n \text{ odd and } n \geq 1.$$

When $\Delta B \neq 0$, the perturbation series converge to equations (19).

3. Response functions of the system 'driven' by different basic excitations

The generalised imaging equation, (18), describes the NMR system's response to a r.f. pulse. We shall briefly formulate the response functions for the different excitations discussed in § 1.4. The general principle to be noted here is that when r.f. pulses affect the response $M(t)$ through the aperture function $F(\mathbf{r})$, the gradients modify the response through the phase term $\exp[i\gamma \mathbf{G}(\mathbf{r}) \cdot \mathbf{r}]$. The ultimate resolution is therefore affected by both functions, though primarily by the gradient. The response functions for the various excitations follow.

This corresponds to $F(\mathbf{r})$ being a constant over the sample space. Geometrically, this implies that $B_1 \gg G_x L$, $t_p \ll T_2$, T_1 and $1/\gamma G_x L$, and $F(\mathbf{r}) = -i$, resulting in

$$m(t) = K \int_V \rho(\mathbf{r}) \exp(-i\pi/2) \exp[i\gamma G(\mathbf{r}) \cdot \mathbf{r}t] dV. \quad (23)$$

3.2 90° and 180° narrowband pulses

These pulses are primarily designed for 'slice' selection in the specimen being imaged. The condition here is $B_1 \cong G_x x$ for $x < L$, $t_p \ll T_1, T_2$ and $t_p \cong 1/\gamma G_x L$. For rectangular B_1 -pulse, $F(x)$ has the form shown in (17).

3.3 Readout gradient

This is applied following a non-selective r.f. pulse, to effect the readout of the FID . The response function, or imaging equation, is

$$m(t) = \int_V \rho(\mathbf{r}) F(\mathbf{r}) L(\mathbf{r}) \exp[i\gamma G(\mathbf{r}) \cdot \mathbf{r}t] dV,$$

which is essentially a free evolution of the magnetisation in the absence of the r.f. excitation.

3.4 Pulsed gradient

The duration of the field gradient pulse is shorter than $1/\gamma G_x L$, so that the magnetisation is constant over the interval τ and

$$m(t) = K \int_V \rho(\mathbf{r}) \exp[i(\gamma G(\mathbf{r}) \cdot \mathbf{r})\tau] dV.$$

This is the key operative equation in Fourier zeugmatography (Kumar *et al* 1975).

4. Reception of the response signal: The NMR receiver

The magnetisation $m(t)$ described by (18), which is our system's response signal, is picked up by a coil. The induced e.m.f. is given by Faraday's law, expressed in the form

$$\varepsilon = -\frac{\partial}{\partial t} (\mathbf{B}_1 \cdot \mathbf{M}_L(t)), \quad (24)$$

using the principle of reciprocity (Hoult and Richards 1976). Here $\mathbf{B}_1$ denotes the magnetic field produced by a unit current in the coil (assumed homogeneous over the specimen volume), and $\mathbf{M}_L(t)$ is the magnetisation in the laboratory frame, related to $m(t)$ by

$$\mathbf{M}_L(t) = m(t) \exp(i\omega_0 t),$$

and therefore the induced e.m.f., (24), is re-written as

$$= AB_1 \omega_0 \operatorname{Re} \left[\left(\int_x M(x) \exp(i\gamma G_x x t) dx \right) \exp(-i\pi/2) \exp(i\omega_0 t) \right],$$

where $M(x) = F_{xy}(x)M_0(x)L(x, t)$ is in general complex,

$$M(x) = M_R(x) - iM_I(x).$$

Quadrature detection with reference signals $\cos \omega t$ and $\sin \omega t$, including low-pass filtering (LPF), gives

$$s_c(t) = \frac{AB_1 \omega_0}{2} \operatorname{Re} \left[\int M(x) \exp(-i\pi/2) \exp[i(\omega_0 + \gamma G_x x - \omega)t] dx \right],$$

and

$$s_s(t) = \frac{AB_1 \omega_0}{2} \operatorname{Im} \left[\int M(x) \exp(-i\pi/2) \exp[i(\omega_0 + \gamma G_x x - \omega)t] dx \right]. \quad (25)$$

Considering that in our experiments the detector reference ω is fixed, ($\omega_0 - \omega$) $\Delta \gamma G_x (L/2)$, it can be seen that $s(t)$ ($\Delta s_c(t) - i s_s(t)$) may be Fourier-transformed to obtain $M(x)$. The phase introduced is in general different from $\pi/2$ due to the contribution from the receiver, and has to be corrected.

A special case of (25) arises when $F(x) = -i$, $L(x)$ is constant over x , and $\omega = \omega_0$. Here $s_c(t) = -\operatorname{Re}[\mathcal{F}^{-1}(M_0(x))]$, and $s_s(t) = -\operatorname{Im}[\mathcal{F}^{-1}(M_0(x))]$. This corresponds, of course, to a 1-D projection of the spin image $\rho(xyz)$.

The other situation encountered is $F(x) = F_x(x) - iF_y(y)$ and $L(x)$ constant over x . This represents a *selective pulse excitation*, where $F_{xy}(-(x+x_1)) = -F_{xy}^*(x+x_1)$, i.e., case of a conjugate skew-symmetric aperture, while $M_0(x)$ is constant over $F(x+x_1)$. x_1 is related to ω (the operating frequency of the transceiver) by $\omega = \omega_0 + \gamma G_x x_1$.

In most modalities the signal is observed in the presence of a readout gradient, representing a combination of the two cases considered above.

4.1 Noise considerations and spectrometer 'figure of merit'

In addition to the FID, noise gets coupled to the system at various stages of the receiver, which degrades the quality of the spin image.

The source of noise is predominantly thermal, and may be assumed to be white Gaussian centred at the operating frequency. For the receiver bandwidth larger than the signal bandwidth (a condition pertinent to our spectrometer design), the noise is assumed to be a bandpass, white Gaussian process. Defining $n_c(t)$ and $n_s(t)$ as the quadrature noise components, $K_{sc}(\tau)$ (the cross-correlation) is zero, as the spectrum of $n(t)$ is symmetric about the carrier. For a real function $M_0(\omega(x))$, $\mathcal{F}^{-1}(S_c(t) - i s_s(t))$ is real; and the reconstructed image is $M_0(\omega) + N(\omega)$, where $N(\omega) = \operatorname{Re}(N_c(\omega)) + i \operatorname{Im}(N_s(\omega))$. In general, where $M_0(\omega)$ is complex, the image may be defined as $M_0(\omega)$ and the noise will be a Rayleigh-distributed random variable for any ω .

The signal-to-noise ratio (S/N), or 'figure-of-merit', may now be evaluated for the bandpass signal $f(t)$ (i.e., the signal is assumed to be time-limited by observation). For

$M(x) = M_0$, a constant,

$$\begin{aligned} f(t) &= \omega_0 B_1 A \operatorname{Re} \left\{ \int_{-L/2}^{L/2} [\exp(i\gamma G_x x t) dx] \exp(i\omega_0 t) \right\} \\ &= \omega_0 B_1 A L \left(\frac{\sin \gamma \frac{G_x L}{2} t}{\gamma \frac{G_x L}{2} t} \right) \cos \omega_0 t. \end{aligned} \quad (26)$$

The signal is gated 'on' from $t = 0$ (or actually t_p , which is *small* compared with $1/\gamma G_x L$ and T_2). The energy, E_s , in the signal envelope is given by

$$\begin{aligned} E_s &= \int_{-\infty}^{\infty} \omega_0^2 B_1^2 V^2 \frac{\sin^2 \gamma \frac{G_x L}{2} t}{\left(\gamma \frac{G_x L}{2} t \right)^2} dt \\ &= \omega_0^2 B_1^2 V^2 \pi T_2^*, \left(T_2^* \sim \frac{1}{\gamma G_x L} \text{ for strong gradients} \right). \end{aligned} \quad (27)$$

From (27), the maximum S/N obtainable is

$$E_s/N_0 = \omega_0^2 B_1^2 V^2 \pi T_2^*/N_0, \quad (28)$$

where N_0 is the white noise power spectral density (if the signal is known *a priori*). This ratio, then, is used as a representative figure-of-merit, as it is based on the assumption that $M(x) = M_0$. Though the spin density variation, $\rho(\mathbf{r})$, and the relaxation time variations $T_1(\mathbf{r})$ and $T_2(\mathbf{r})$ carry the imaging information (as contrast), these variations are usually small in a sample and hence the bulk sensitivity of the system is indicated by (28), which compares well with the E_s/N_0 derived earlier for a pulsed NMR experiment (Ernst and Anderson 1966).

The overall system identification in terms of system-input and system-response is depicted in figure 5.

5. Spectrometer design considerations

This section considers various aspects of design strategy we have adopted in configuring a 15 MHz proton imaging spectrometer for studying multiphase bio-samples. The block schematic of the system, shown in figure 6, is broadly categorised into (i) the r.f. probe (ii) the r.f. pulsed power transmitter and receiver (transceiver), (iii) magnetic field and magnetic field gradient control, and (iv) signal acquisition and averaging.

5.1 The sample coupling r.f. probe

This is the 'heart' of the system, acting as an interface between the specimen under study

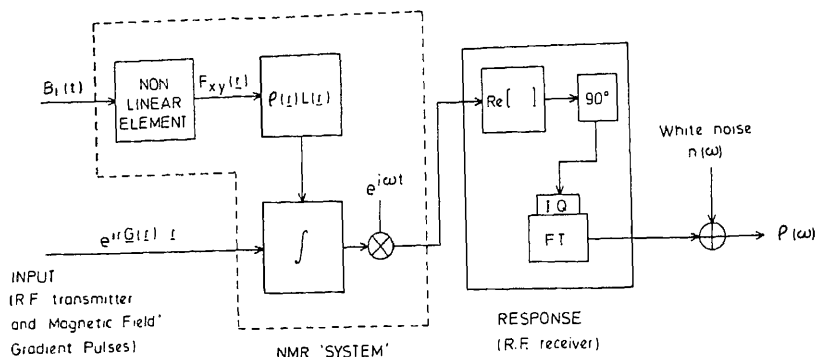


Figure 5. Overall system identification in terms of input (r.f. transmitter pulse and the magnetic field gradient) and response (magnetisation) as seen by the r.f. receiver. In the receiver section, $\text{Re}[\]$ denotes the real, or in-phase, signal response component, and IQ denotes the imaginary, or quadrature, response component. $n(\omega)$ denotes white noise at the output.

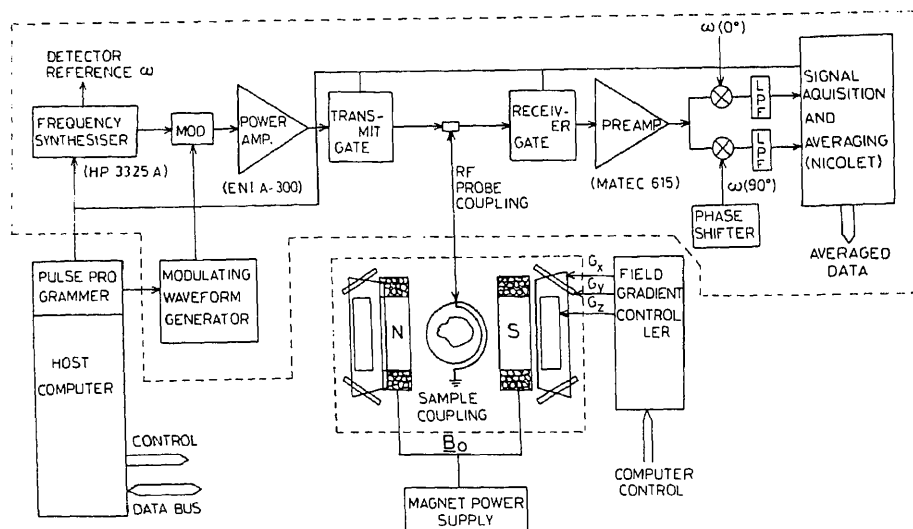


Figure 6. Block schematic of our NMR imaging spectrometer. The dotted section corresponds to the overall 'system' identified earlier.

loop 'pairs' are known to be used in 'crossed coil' arrangements. As the solenoidal and saddle-shaped coils produce linearly polarised B_1 fields, only half the current is effective for sample excitation.

The performance of the coil is measured in terms of r.f. field uniformity and coupling efficiency (related to S/N). As these requirements conflict, a trade-off is employed. For example, the solenoidal configuration has a 10 dB S/N advantage over the saddle-shaped

Here the essential features of the transmitter section are (a) generation of pulsed r.f. from a programmer unit based on an 8253 on-board counter chip of a commercial microprocessor (VMC-85); pulse timing sequences (see Dick 1976; Adduci and Gerstein 1979) are derived from this chip, (b) high pulsed power from the transmitter amplifier, (c) impedance matching with the 'load' (which is the sample coil resonant circuit), (d) small post-transmit 'deringing' time τ_d , (e) a short rise-time (or large bandwidth) power amplifier, (f) modulating signals for selective pulse excitations, and (g) a 'transmit' switch offering low 'on' attenuation and high 'off' isolation, to decouple transmitter noise from the sample coil during reception of FID.

In the receiver section, the following are incorporated: (a) a low noise-figure preamplifier, (b) efficient noise and signal power matching of the source (the sample coil) with the receiver preamplifier, (c) quadrature demodulator/detector for recovering the baseband signal (with an anti-aliasing filter), and (d) r.f. switches with high isolation to protect the receiver from high-power r.f. pulses and low 'on' attenuation, and shot-noise contribution, during signal reception.

The specifications for an ENI A-300 broadband power amplifier and a 'Matec' r.f. preamplifier-receiver have been assumed in our design of the transceiver circuit. In table 1 are listed the parameters for the system we have developed. The deringing time, τ_d , is estimated for the worst-case values of T_2^* ($\sim 1/\gamma G_x L$) and T_2 . The resistance (R), inductance ($\mathcal{L}$), quality factor (Q_c max.) and the distributed capacitance (C_d) of the solenoidal coil used in our work are given along with peak (I_p) and average (I_{av}) current and the B_1 requirements for $t_p \sim 5 \mu\text{s}$ and $\phi = 90^\circ$.

5.3 Magnetic field and gradient control

For a proton resonance frequency of $\sim 15 \text{ MHz}$ the B_0 field falls in the $0.3T^*$ range, and this is supplied by a research electromagnet whose central field has been shimmed

Table 1. NMR imaging spectrometer: Important design parameters.

Parameter	Value
T_2^* (for $5 \mu\text{Tcm}^{-1}$)	$2.27 \times 10^{-4} \text{ s}$
T_2	$50 \mu\text{s} - 5 \text{ ms}$
T_1	$5 \text{ ms} - 500 \text{ ms}$
τ_d	$\leq (50 \times 10^6 / 100) \cong 0.5 \mu\text{s}$
$R^{(a)}$	$0.011 \text{ n}^2 \text{ ohms}$
$\mathcal{L}$	$0.027 \text{ n}^2 \mu\text{H}$
Q_c (max)	200
C_d	10 pf
I_p	$106/n \text{ amp.}$
I_{av}	$(1/\sqrt{2})(106/n) \text{ amp.}$
$B_1^{(b)}$	$2.22 \times 10^{-5} \text{ nT}$

^(a) n = Number of turns of probe coil.

^(b) B_1 is calculated for $\phi = 90^\circ$, $t_p = 5 \mu\text{s}$.

to about 10 parts per million homogeneity with ferromagnetic plating and electrical compensation coils.

For the gradient coil system, three pairs of coils are used for the x , y and z directions. The x and y gradient coils are of saddle-shaped geometry, as this is known to give acceptable higher-order spatial field nonlinearity. In the z -direction, we employ a Helmholtz pair mounted on the magnet pole-faces. These three sets of coils are energised by a microprocessor-controlled current driver built from a low-drift operational amplifier (LM 308). Typical gradients of $10\text{--}50\ \mu\text{T cm}^{-1}$ (with $\sim 1\%$ linearity over the sample volume) are achievable, enabling an upper limit image resolution of 1 mm (corresponding to a frequency resolution of 200 Hz). The ampere-turns (A_T) required for $50\ \mu\text{T cm}^{-1}$ gradient is $12\ A_T$ for Helmholtz pair with a diameter-to-length ratio (D/l) = 1 and $19\ A_T$ for $D/l = 0.5$. Since the latter ratio is optimum in the sense that the second and third field derivatives at the centre of the coil are equal to zero, we have preferred $19\ A_T$ in our design.

The theoretical S/N (equation (28)) is $E_s/N_0 = 70\ \text{dB}$ for $T_2 = 2.27 \times 10^{-4}\ \text{s}$ and $55\ \text{dB}$ for $T_2 = 50\ \mu\text{s}$ for whole-sample excitations. This corresponds to the FID from a single image projection. A set of six to eight projections in a plane are tractable for reconstruction of the image, considering the software complexity. The resulting E_s/N_0 is $77\ \text{dB}$ (taking into account signal averaging). The corresponding (0 dB S/N) resolution is $\Delta V = 5.32 \times 10^{-10}\ \text{m}^3$ (or $\Delta x = 1\ \text{mm}$). Our instrumentation is limited to off-line projection reconstruction as the operational modality.

5.4 *Signal acquisition and sampling*

The FID after demodulation is recorded digitally. The minimum sampling rate F_s is determined by the Nyquist criterion, $F_s > 2 \times [\text{signal bandwidth}]$ where the bandwidth may be given by $2 \times 10 \times (1/2\pi T_2)$, while the number of 'samplings' per unit bandwidth is determined by resolution considerations. The intrinsic resolution is considered to be $(1/t_w)$ where t_w is the acquisition-time window. The FID corresponding to our simple case of 1-D projection is written as $V_s = V_0$ since $(\gamma G_x L t / 2\pi)$. Calculation of the time at which V_s would roughly fall to the rms noise voltage should yield a lower limit to the observation time.

In our spectrometer system, a 'Nicolet 1174' high speed ($1\ \mu\text{s}$ per point per input) signal digitizer/averager with an 8-bit analogue-to-digital resolution is used, which acquires and stores the time-averaged information on the point-by-point FID data samplings. The 1174 memory stores $4K \times 20$ bits of digitised signal. The stored data are transferred to a DEC 1090 computer for off-line image processing.

6. Conclusions

We have discussed NMR imaging from the viewpoint of system design. Models based on Bloch equations and rotating frame formalism provide a useful mathematical description of different NMR imaging schemes. The response, namely, the magnetisation $M_{xy}(t)$, is linearly related to the system identification function $\rho(\mathbf{r})L(\mathbf{r}, t)$ while the r.f. excitation affects the system nonlinearly and appears as an 'aperture' function in the imaging equation. Solution of the imaging equation for a rectangular r.f. pulse is possible in closed form, while for other pulses it is obtained numerically. In addition,

approximating the system by the linear term $M_{xy}(t)$ in a perturbation expansion. Spectrometer design considerations indicate that the resolution is limited by noise at the detection stage, and that the solenoidal r.f. probe configuration has a significant S/N advantage over the saddle-shaped configuration, although the r.f. field homogeneity is better in the latter. In the case of our NMR imaging spectrometer developed for studying multiphase biospecimens, a 1 mm image resolution is feasible with a gradient of $\mu\text{T cm}^{-1}$, assuming a 200 Hz frequency resolution and signal averaging.

knowledge

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Recent trends in the study of switching processes in ferroelectrics

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Abstract. Several ferroelectrics and materials showing ferroelectric-like switching behaviour have been widely investigated and both an exponential or power law of t_s on E have been reported. However, the mechanism of polarization reversal and domain dynamics show a complexity that makes it difficult to generalize and draw a common rule for all types of ferroelectrics. Radiation damage, internal biasing fields and defects alter the switching characteristics and in this review including some of the work of the authors on TGS, sodium nitrite DSP etc, the present trends in the study of switching and the electroluminescence during switching have been discussed.

Keywords. Polarization reversal; radiation damage; ferroelectrics; switching processes.

1. Introduction

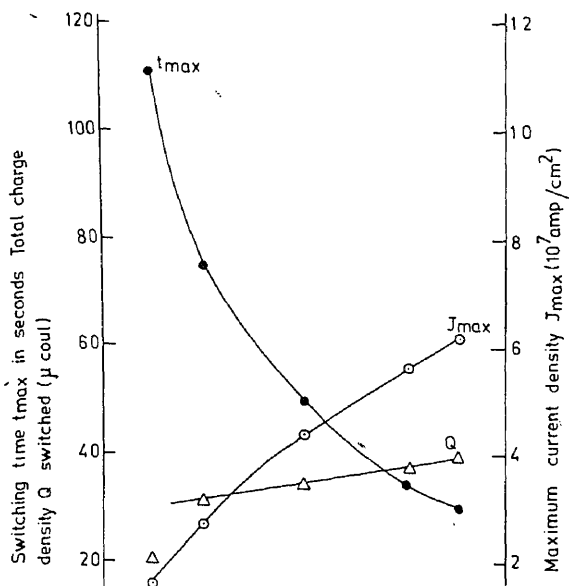
The characteristic property which distinguishes a ferroelectric is its macroscopic polarization which can be switched or reoriented by the application of an appropriate external electric field. This property makes ferroelectrics very attractive candidates for memory device applications where one of the prerequisites is a bistable material property which can be switched between two well-defined states. In addition to this, the recent discovery of the large coupling between optical and electrical properties in some of the ferroelectrics has revived interest in the use of these ferroelectrics in optical device applications. In these materials, an optical property such as refractive index, birefringence or the sense of optical rotation can be controlled by the application of an external electric field. In spite of such potential applications existing for ferroelectric materials, several inherent disadvantages have precluded their widespread use. Most ferroelectrics do not possess a well-defined coercive field in contrast to ferromagnets. This was due to the fact that in ferroelectrics the polarization could be switched by even very small electric fields applied over a sufficiently long time. Also devices based on such ferroelectric materials would not be immune to noise signals. Further subjecting the ferroelectric material to repeated switching by an external field tends to fatigue the material and causes the coercive field to rise. The response to applied field also slows down.

A more detailed study of the switching process in ferroelectrics is therefore desirable to understand the mechanism of the processes and also to produce ferroelectrics with improved properties. The experimental methods for studying the switching process are based on a method originally developed by Merz (1954). In this method, a train of square pulses is applied to the sample in the form of a capacitor. Information about the switching process can be obtained from the switching current transient flowing in the sample during the switching process. An important development has been the use of computers for the acquisition and analysis of data obtained from switching process studies (Montoto and Jacque 1978).

The presence of defects originating during the material preparation, radiation damage or due to doping can alter the switching processes in ferroelectrics. The presence of defects stabilizes a well-defined coercive field. In analogy to ferromagnetic materials, the switching in ferroelectrics proceeds through the motion of domain walls enlarging the size of favourably oriented domains in the material. The domain wall motion is clamped by the defects present in the material. Thus in order to elucidate the role of the defects on the switching process, switching studies on typical ferroelectrics such as rgs have been carried out. In addition to investigating the switching processes in materials such as gadolinium molybdate and lead germanate, switching processes in liquid crystals and polymers which show ferroelectric-like behaviour have also been studied. The electroluminescence observed during switching has also been investigated (Montoto and Jacque 1978). This has been verified to occur from the recombination of uncompensated charge in the surface layers.

2. Theory

The macroscopic polarization of ferroelectric can be switched or reoriented by an external field. During the switching process, a transient current flows in the sample. The transient has a sharp initial spike (duration $\sim 0.1 \mu\text{sec}$) followed by a hump whose peak appears after a time interval called switching time t_s , ranging from microseconds to minutes from the initial point of the transient. The spike occurs due to stray capacitance inherent in the apparatus used to excite and detect switching. The



electric field, the ferroelectric material, the temperature, and the applied electric field E is described by

$$1/t_s = \gamma E \exp(-\alpha/E), \quad (1)$$

$$1/t_s = \frac{1}{t_m} \exp(-\delta_t/E). \quad (2)$$

Relation (1) has been used by Pulvari and Kuebler (1958) while the second has been derived from Miller and Weinreich (1960). Equation (2) is applicable in the low electric field region when t_s exhibits a non-linear relationship. Relation (2) can be used both in the low and high E regime. In the high E regime an additional relation (Merz 1954).

$$1/t_s = BE^n \quad (3)$$

can also be used. The quantities α , δ_t are called activation fields which can be related to the internal biasing fields and the coercive field of the crystal. The activation fields increase with decrease in temperature, increase in pressure and also whenever defects are present in the ferroelectric. This increase presages a slowing down (rise in t_s) of the switching process. Further

$$\gamma = \mu/d,$$

where μ is the mobility and d is the sample thickness. μ can be identified with the spread of the switching process over the volume of the ferroelectric.

The quantities α , δ_t , μ are uniquely defined for a single temperature, pressure, sample material etc. The activation fields are defined with respect to the applied field.

The temperature-independent activation energies E_a are defined by relations of the type,

$$1/t_s = A \exp(-E_a/kT), \quad (4)$$

E_a can be evaluated as the slope of a plot of $\ln(1/t_s)$ vs $(1/T)$.

The activation field is a measure of the constraints encountered by the individual domain polarizations in switching in response to the applied field. As the temperature moves away from the transition temperature into the ferroelectric region, some of the domain polarizations get clamped. The presence of defects also produces similar effects. Further, in the transition from the para- to ferroelectric state, there can be drastic changes in the molecular environment as first order transitions are always accompanied by latent heat changes and molecular rearrangement. Thus for first order ferroelectrics an internal biasing field can be present. This denotes the difficulty encountered by the individual domain polarizations in switching. Sometimes the internal biasing fields can be so high that switching occurs only in very high electric fields with very low values of macroscopic polarization. In such cases switching can be observed only in a region close to the transition temperature, and only with the application of very high fields at lower temperature.

3. Switching studies in individual ferroelectrics

3.1 Polyvinylidene-di-fluoride (PVDF)

PVDF exists in various polymeric phases. The most common polymorph α is nonpolar. Uniaxial drawing transforms phase into β phase which is polar and the molecular

adopt a planar zig-zag conformation. The molecular dipoles inherent to the monomer unit ($-\text{CF}_2-\text{CF}_2-$) are all aligned in the same direction perpendicular to the chain axes. Polarization reversal in PVDF was originally considered to be a slow process on account of the poling conditions employed by Kawai (1969), who used long time (~ 30 min) and high temperature ($> 100^\circ\text{C}$).

Using these poling conditions, Buchman (1973) made the first switching studies on PVDF using the Merz method. He observed slow switching processes (several minutes) at temperatures above 100°C and in low fields below 15 MV/cm . He inferred that the slow switching process arose from the long-chain nature of the molecules. The results of Buchman (1973) are presented in figures 1 and 2.

Later investigations by Furukawa and Johnson (1983) and Takase and Odajima (1983) have shown that switching can occur at lower temperatures (20°C to -100°C) at much higher fields ($\sim 200\text{ MV/cm}$) and can be a much faster process (several microseconds).

Dvey-Aharon *et al* (1981) have theoretically investigated the switching process in PVDF in terms of the propagation of a kink of rotation or a solitary wave along the molecular chain. They have shown that a model involving 60°C rotation of the chains yields results in conformity with experiment. According to this model the individual domain polarizations are out of alignment by 60° from those of adjacent domain polarizations. Poling and switching in the presence of an applied field proceed through the nucleation of domains with favourably oriented domains by propagation of 60° rotations of chains in unfavourably oriented domains.

Takase and Odajima (1982) evaluated the activation field as 1.3 GV/m (at 20°C) and the activation energy as 0.63 eV . These results are in agreement with those of Furukawa and Johnson (1983), which are presented in figure 3. The activation field in this case varies from 1.1 GV/m (20°C) to 1.9 GV/m (-60°C).

In PVDF the large value of the activation field suggests that the switching process occurs mainly in the field range where $1/t_s$ has an exponential dependence on E . The low

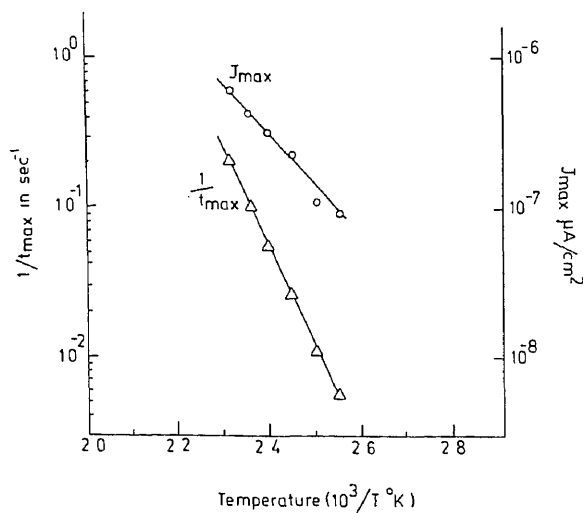


Figure 2. Variation of switching time t_s and current density with temperature in polyvinylidene fluoride (PVDF).

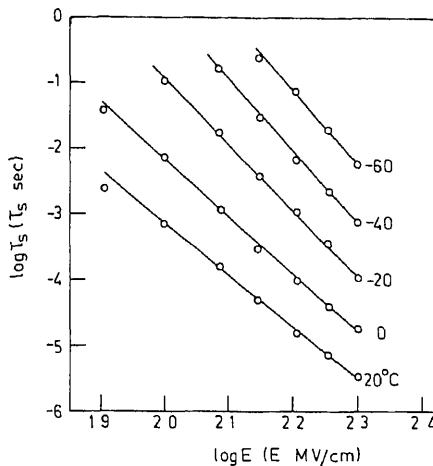


Figure 3. Variation of switching time $t_{\max}$ and current with electric field at various low temperatures for PVDF (from Takase and Odajima 1982)

field range has been identified (Merz 1954) as the region in which nucleation of favourably oriented domains occupies most of the switching time. In PVDF, switching cannot be observed below a threshold field at lower temperatures (120 MV/cm at 20°C). At very low fields, switching can be observed only at temperatures above 100°C. This threshold effect and large activation fields arise from the energy of formation of the domains by 60° rotation of the long chain molecules.

3.2 Liquid crystals and related compounds

The first experimental study of ferroelectric-like switching behaviour in a material which exhibits liquid crystalline behaviour was by Williams and Heilemeier (1966). They studied the switching behaviour in azoxyphenetole and azoxyanisole, which exhibit nematic liquid crystalline phases. One interesting observation reported by them was that the ferroelectric switching behaviour was observed both in the liquid crystalline and in the isotropic liquid phase existing above the liquid crystal isotropic liquid phase transition.

Martinot Lagarde (1977) reported the observation of ferroelectric-like switching behaviour in the smectic (phase of HOBA CPC (P-hexyl-oxy benzylidene-P'-amino-2-chloro-propyl-cinnamate). Figure 4 shows the variation of polarization charge Q with temperature.

The smectic phase of a liquid crystal can be characterized by a director $\bar{n}$ which is at an angle to the normal to the layers making up the smectic phase. In a chiral smectic, $\bar{n}$ precesses about the layer normal and thereby determines the pitch which is 1–10 μm usually. Cladis *et al* (1983) have studied switching in a chiral smectic. The chiral smectic has a permanent polarization $\bar{P}$ perpendicular to both $\bar{n}$ and the layer normal (Meyer 1977). When an electric field E is applied to the sample of chiral smectic, domains with polarizations $\bar{P}$ parallel to E grow through wall motion in the form of solitary waves—called soliton motion. Walls separate regions with $\bar{P}$ oriented parallel and antiparallel to E . The regions with unfavourable $\bar{P}$ never vanish completely; there are small regions

state and the final state with most of the $\vec{P}$ parallel to E , has a $1/E$ dependence. In the case of switching in a chiral smectic, threshold field effect is not observed.

Brand and Cladis (1984) reported the observation of switching behaviour in the smectic $-X$ phase. They studied the switching behaviour in smectic X phase of $8SI^* - S-(+)-(4-2'-methylbutyl)$ phenyl 4'-A-octyl biphenyl-4-carboxylate. A linear relationship between V and the sample temperature T (figure 5) was observed. Here V is the applied voltage and t is the switching time between the non-oriented and oriented states.

Azoxybenzene is the first member of the homologous series to which azoxyphenetole and azosyanisole belong. Azoxybenzene is an isotropic liquid above 38°C . Ferroelectric-like switching behaviour was observed in the isotropic liquid phase (Ravi and Narayanan 1982). It was observed that the switching time depended linearly on the applied field (figures 6 and 7) and that the switching process was slower than in triglycine sulphate for similar values of E .

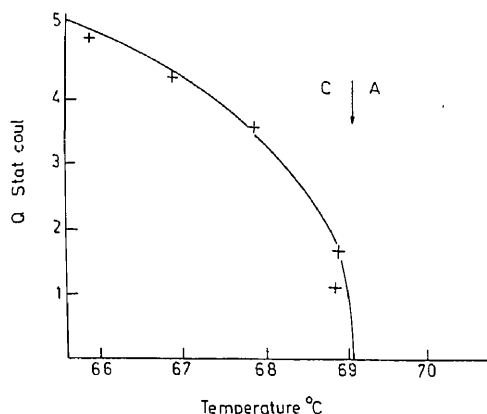
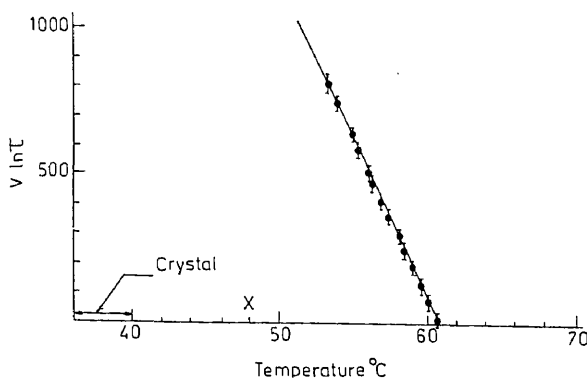


Figure 4. Variation of polarization charge Q with temperature in HOBACPC (from Martinot Lagare 1977)



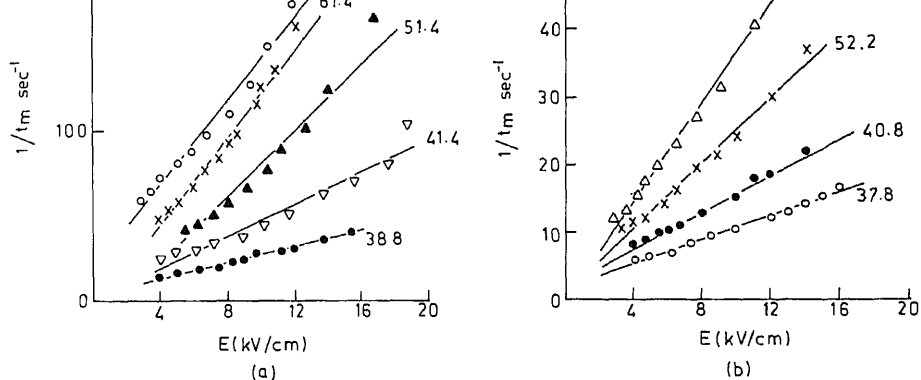


Figure 6. Variation of switching time with applied field at various temperatures in azoxybenzene (from Ravi and Narayanan 1982)

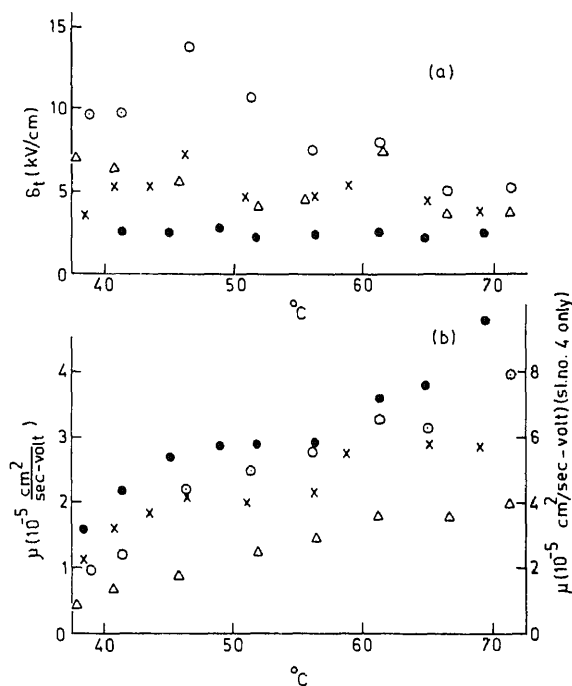


Figure 7. Variation of σ_t and μ with temperature and thickness in azoxybenzene (from Ravi and Narayanan 1982)

3.3 Single crystals

3.3a Gadolinium molybdate: The ferroelectric switching behaviour of gadolinium molybdate was studied by Kumada (1969, 1972) and the data are given in figures 8 and 9.

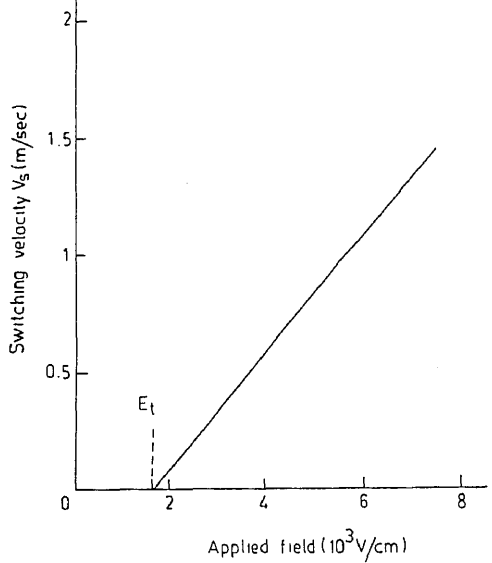


Figure 8. Variation of switching time with applied field in gadolinium molybdate (from Kumada 1972)

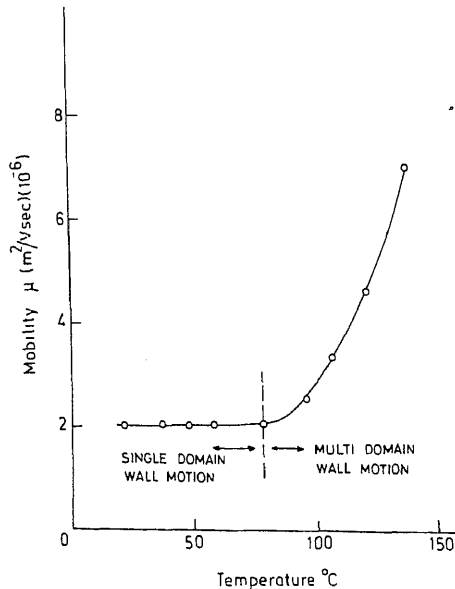


Figure 9. Variation of mobility μ with temperature in gadolinium molybdate. (from Kumada 1972)

3.3b *Lead germanate*: Iwasaki *et al* (1971, 1972) studied the switching behaviour of lead germanate. Lead germanate exhibits optical activity in the ferroelectric phase. The

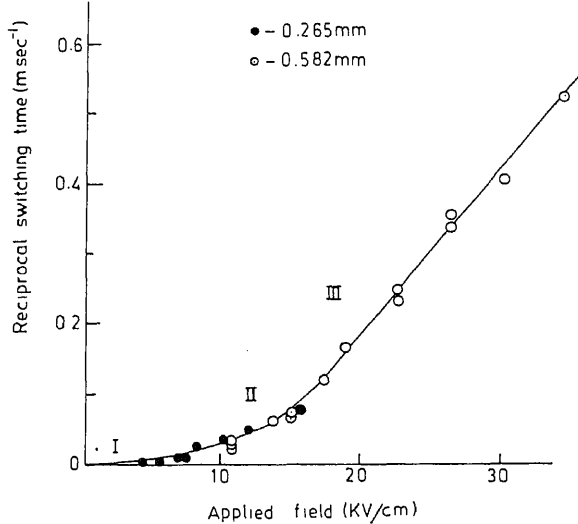
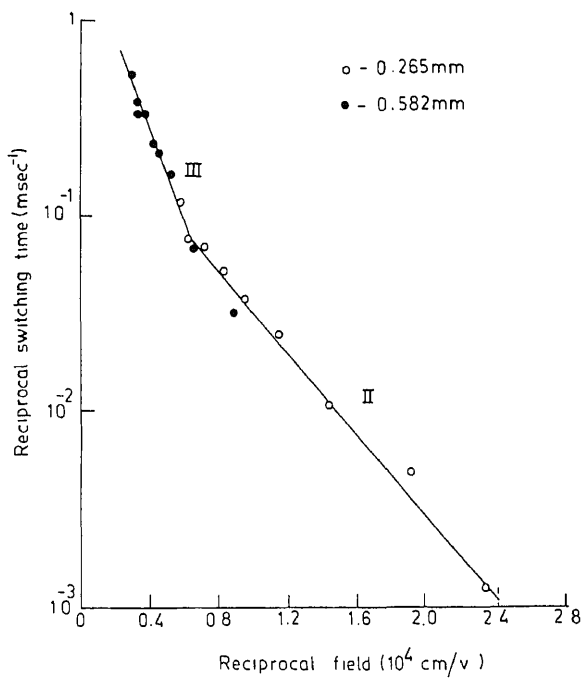


Figure 10. Variation of switching time in regions I, II and III in lead germanate (from Iwasaki *et al* 1972)



dependence of the switching time t_s on E in three regions:

- (i) Region I (low field).
- (ii) Region II (moderate applied field),

$$1/t_s = 1/t_\infty \exp(-\alpha/E), \alpha = 2.5 \times 10^4 \text{ V/cm.}$$

- (iii) Region III (high field)

$$1/t_s = A \exp(-\beta), \beta = 2.7; A \text{ is a constant.}$$

The data for variation of t_s on E is shown in figures 10 and 11.

3.3c Dicalcium strontium propionate (DSP): DSP is an improper ferroelectric below 8.5°C. Ferroelectric switching behaviour of DSP has been studied (Ramanath, Ravi and Narayanan 1982). It was found (figures 12–13) that the switching time depends linearly on the applied electric field E and that the switching process is slower than in triglycine sulphate for comparable values of E , in the temperature range in which the switching behaviour of DSP was studied.

3.4 Irradiated single crystals

3.4a Triglycine sulphate: The switching process in single crystals of triglycine sulphate radiation damaged by x-rays and gamma rays was investigated by Ravi and

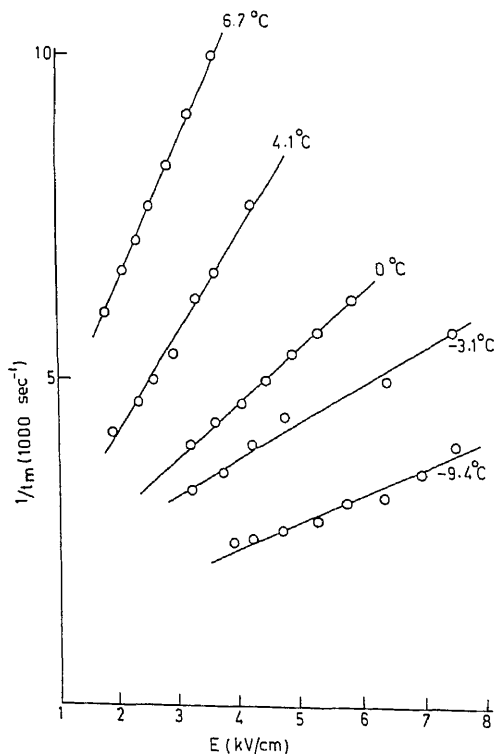


Figure 12. Variation of switching time with applied field at various temperatures in dicalcium strontium propionate (dsp). (From Ravi and Narayanan 1982)

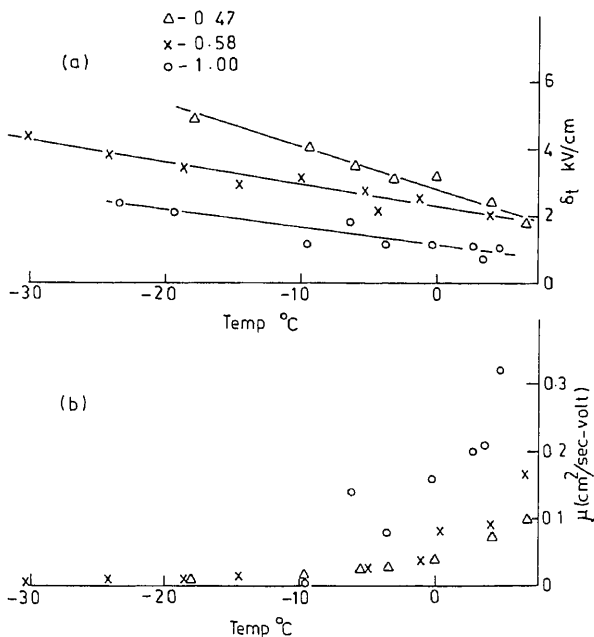
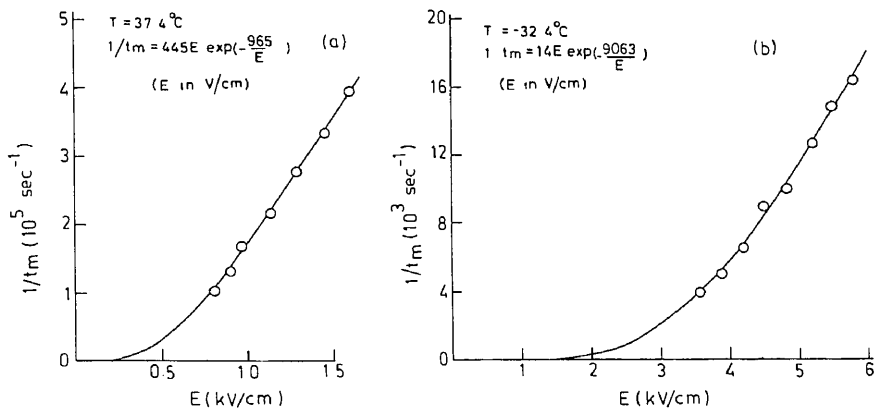


Figure 13. Temperature variation of mobility μ and activation field δ_t in DSP (from Ravi and Narayanan 1982)

Narayanan (1982). It was found that the switching time shows an exponential dependence on the applied field E and that there is an increase in the activation field (figures 14–18).

Investigations (Fletcher *et al* 1976a, b) and the structure of irradiated rgs indicate that irradiation brings about changes in the hydrogen bond system of rgs. The nitrogen atom on glycine I in irradiated rgs has only two hydrogen atoms attached to it instead of the three hydrogen atoms in unirradiated rgs. The pseudo-mirror symmetry about



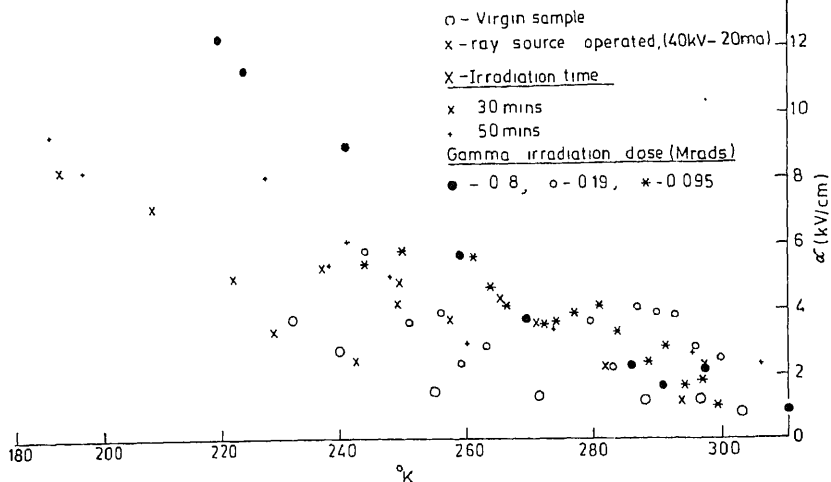


Figure 15. Variation of α with temperature and radiation dose in triglycine sulphate.

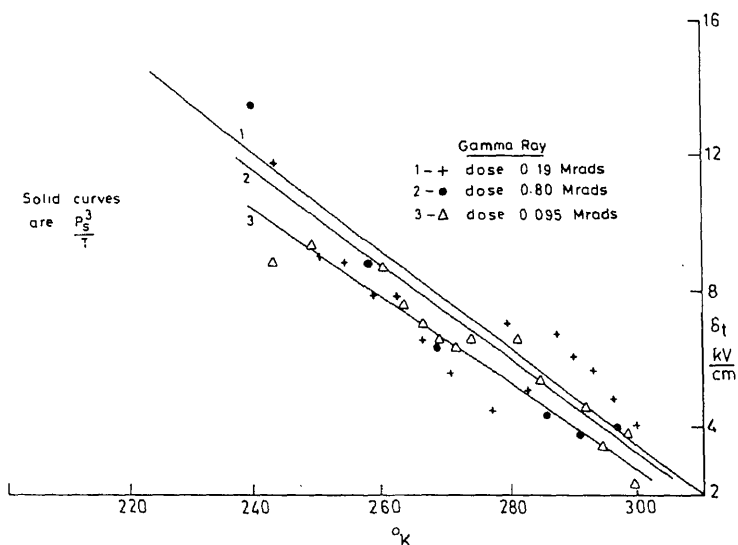


Figure 16. Variation of δ_i with temperature for pure and irradiated triglycine sulphate.

the plane $\bar{Y} = 1/4$ is destroyed and the switching of glycine I is made more difficult, and requires more energy. This is reflected as an increase in the activation fields for irradiated as compared to normal TGS.

3.4b Sodium nitrite: The switching process in gamma irradiated sodium nitrite has been studied (Ravi and Narayanan 1981a) and it has been observed that the switching time shows an exponential dependence on the applied field and that α and δ_i increase (figures 19-21). In sodium nitrate, irradiation is found to produce neutral NO_2 radicals (Gesi and Tokoci 1964). This shows that the switching mechanism is different for irradiated samples.

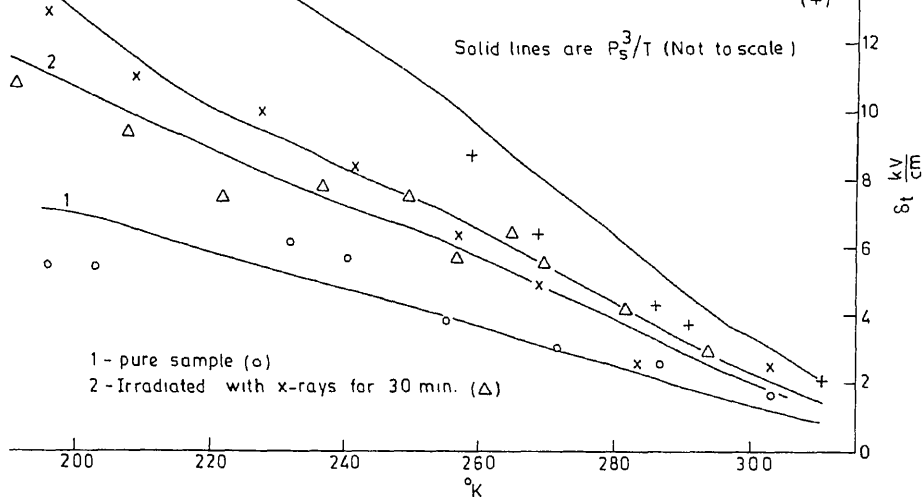


Figure 17. Variation of δ_i with temperature and radiation dose in triglycine sulphate.

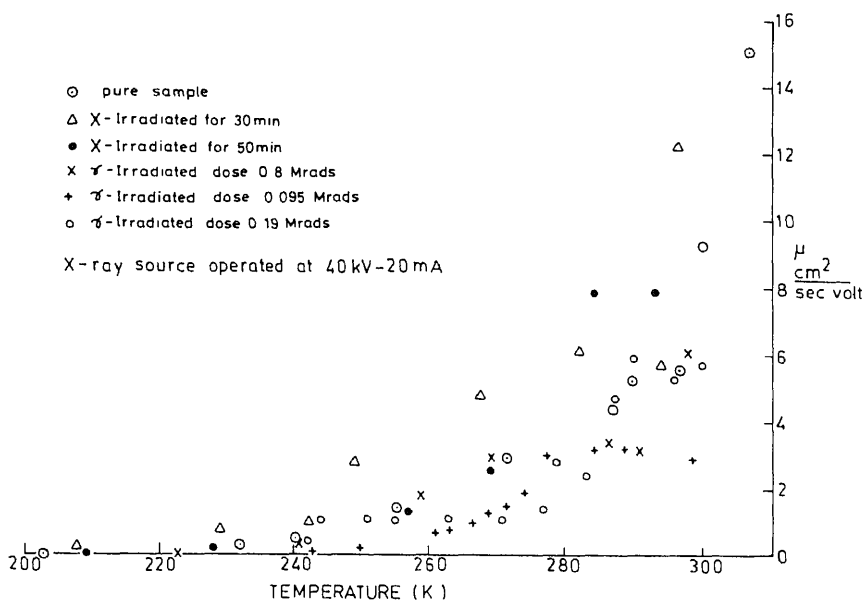


Figure 18. Variation of μ with temperature and radiation dose in triglycine sulphate.

for switching and there is an increase in α and δ_i . The switching process in irradiated crystals is slower and the temperature range for its occurrence is of lesser extent than in unirradiated crystals. The irradiation dose required to produce significant changes in

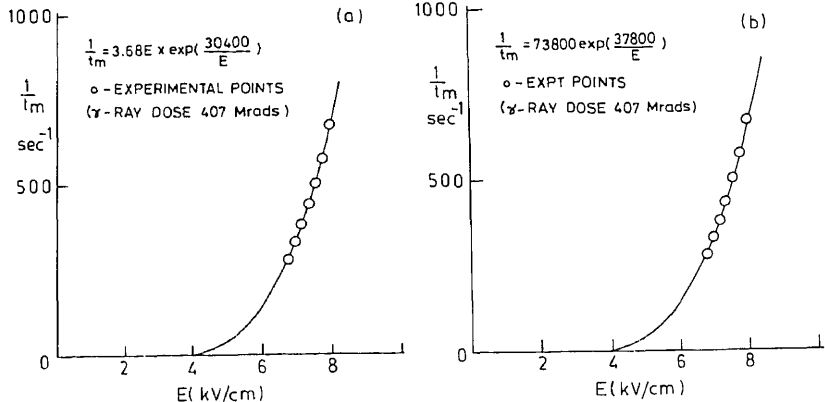


Figure 19. Variation of $1/t_m$ with E according to (a) $1/t_m = \gamma E \exp(-\alpha/E)$ and (b) $1/t_m = 1/t_\infty \exp(-\delta_t/E)$ in sodium nitrite.

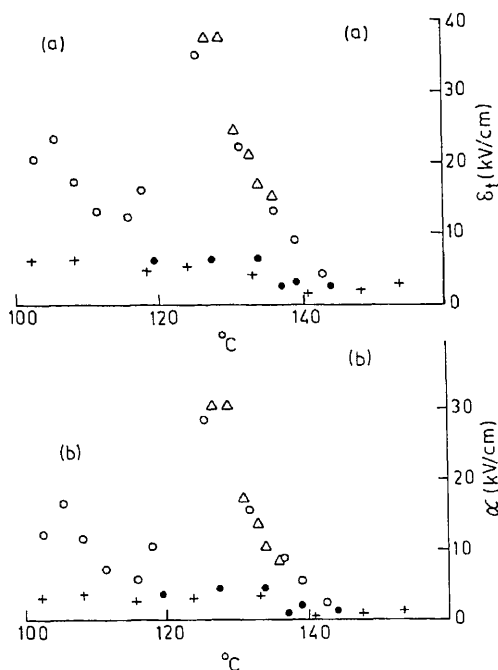


Figure 20. Variation of (a) δ_t and (b) α with gamma radiation dose in sodium nitrite. + = 7.2 Mrads, 0-70 Mrads, 0-100 Mrads, - 407 Mrads.

the switching characteristics of TGS is 0.1 Mrad while for sodium nitrite it is 100 Mrad. The hydrogen bonds of TGS are weaker and require lesser radiation dosage than the largely ionic bonds of sodium nitrite to produce changes in switching behaviour.

4. Electroluminescence during polarization switching

Light emission of electroluminescence has been observed during the polarization

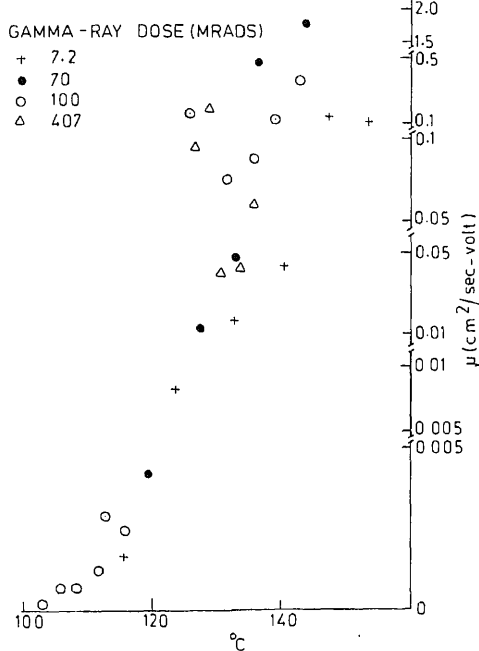


Figure 21. Variation of μ with gamma radiation dose and temperature in sodium nitrite.

Gonzalo *et al* 1980), KNbO_3 (Deshpande *et al* 1977), and $\text{Gd}_2(\text{MoO}_4)_3$ (Flerov and Taran 1979).

Simultaneous observation of the light emission and switching current in low fields showed that the light emission starts when the switching current passes through the peak, which shows that the switching current and light emission are out of phase. At higher applied fields, the current and emission are in phase. The light emission occurs when the electric field in the surface layer is a maximum, i.e. when the voltage drop in the surface layer is largest and when current transient is at its peak. The large electric fields in the surface layers could promote electron injection from the electrodes. Accumulation of uncompensated charge, carried by moving domain walls, in the surface layers can also promote charge injection from the electrodes. Thus it has been suggested that electroluminescence during switching arises from recombination phenomena in the surface layers. Experimental evidence for X-irradiated rgs (Montoto and Jaque 1981) has been shown to fit in with theoretical calculations and this suggests that light emission originates in the surface layers.

Acknowledgement

The authors would like to conclude this article with their tribute to the late Prof. R. Srinivasan with whom one of the authors (PSN) has had the benefit of discussions for over two decades about the correlation between the NMR and EPR studies on ferroelectrics and the static properties, domain structure and light scattering in ferroic

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Structural phase transitions and superconductivity in hexagonal tungsten bronzes

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Abstract. The anomalous behaviour of the superconducting transition temperature T_c as a function of x in M_xWO_3 (hexagonal tungsten bronzes), where $M = K, Rb$ or Cs and $0.16 < x < 0.33$, is explained in terms of structural transitions involving WO_6 octahedral chains which are subject to Jahn-Teller (J-T) effect. Above a critical concentration ($x_c \sim 0.24$) there is cooperative J-T effect resulting in a structural transition. Below this, there will exist only local distortions. The effect of these is to modify the density of states and lead to shifting and splitting of the relevant peaks. It is shown that the density of states profile at the Fermi level controls the superconducting transition temperatures as a function of x .

The conduction electrons in these systems are J-T polarons subject to competition between symmetry-breaking distortion and the band delocalizing effects.

Keywords. Hexagonal tungsten bronzes; Jahn-Teller polarons; superconductivity; structural transition.

1. Introduction

Tungsten bronze with the formula M_xWO_3 , where M represents alkali metal ions, constitute a series of non-stoichiometric compounds and exist in several structures as a function of concentration x of M atoms. These range from cubic to tetragonal (I & II) to hexagonal (Kihlborg 1983). In the present paper, we shall be interested only in hexagonal tungsten bronzes (HTB) which have $M = K, Rb$ or Cs and x can vary from 0.16 to 0.33. These systems exhibit anomalous electrical and structural properties as a function of x and temperature. The superconducting transition temperature T_c as a function of x displays a minimum around $x = 0.25$ in K_xWO_3 and Rb_xWO_3 and in CS_xWO_3 a smooth lowering of T_c on going from $x = 0.20$ to $x = 0.32$ (Stanley *et al* 1979; Skokan *et al* 1979; Cadwell *et al* 1981). The resistivity as a function of temperature shows a local minimum at a temperature T_B (in the temperature range 100 to 300 K) in both K_xWO_3 and Rb_xWO_3 . The value of T_B varies with x . In fact, T_B peaks at the value $x = 0.25$. The Hall and Seebeck coefficients exhibit similar high temperature anomalies (Stanley *et al* 1979; Cadwell *et al* 1981). These anomalies, which depend on the concentration of alkali atoms, suggest some kind of structural phase transitions and phonon softening. Although earlier experimental work using x-ray diffraction did not reveal any clear-cut structural transition, recent neutron diffraction measurements do show evidence of these in Rb_xWO_3 as well as softening of some phonon modes (Sato *et al* 1982, 1983). In order to understand the nature of these phase transitions in HTB, it is essential to have an idea of their structure.

In these systems, an arrangement of octahedra in the ab plane forms the framework of the structure (Magneli 1953; Kihlberg 1983). The packing is such that they leave triangular and hexagonal cages or tunnels (see figure 1). The alkali atoms (M) reside in the hexagonal cages (size about 2 Å). The triangular cages are rather small. At concentration $x = 0.33$ there are two M atoms per unit cell and all cages are filled. For $x = 0.16$ there will be only one M atom per unit cell (50% of hexagonal cages vacant). The electron diffraction and microscopy results on $K_x\text{WO}_3$ by Bando and Iijima (1981) show incommensurate superstructure along the c -axis for $0.24 < x < 0.26$ at room temperature suggesting approximate doubling of the c axis. However, the important point to note is that the original c itself extends over two octahedral layer which is caused by a slight displacement of the W atoms in the HTB structure.

Results of neutron diffraction studies by Sato *et al* (1982) on $\text{Rb}_{0.27}\text{WO}_3$ at 10 K show additional peaks which disappear in the high temperature phase above $T_s = 205$ K. This temperature T_s is in agreement with the temperature T_B connected with resistivity anomaly. The sub-lattice peaks are explained by the ordering of Rb atoms in the c -axis which leads to the doubling of this axis. Yet another ordering of Rb atoms, this time in the c -plane, occurs in the samples with $x < 0.25$. This appears at temperature T_s , which varies from 480 K to 280 K as a function of composition (Sato *et al* 1983).

Perhaps the most important transition observed by this group is the one at 420 K and in the range $0.25 < x < 0.33$ associated with the appearance of (103) reflection. The peak is absent above 420 K. Below this temperature, a softening of the optical phonons at the Γ point takes place. The transition is associated with the distortion of the WO_6 octahedra and is nearly of second order (Sato *et al* 1983). We believe that of the three structural transitions described above, the last one is of crucial importance in determining the superconducting behaviour in these systems. The distortion arises from a Jahn-Teller (J-T) type splitting of the atomic t_{2g} levels of the W atoms.

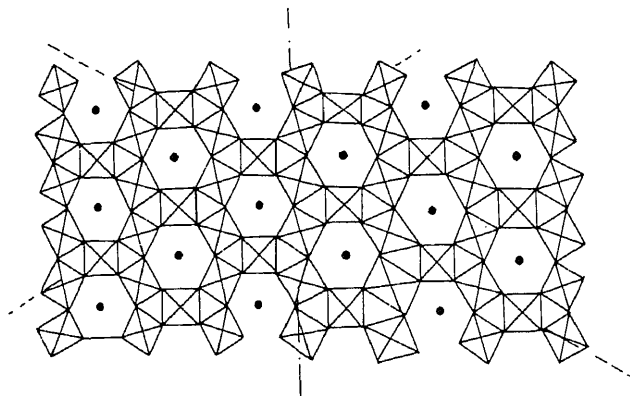


Figure 1. The structure of hexagonal tungsten bronzes ($M_x\text{WO}_3$). The squares represent WO_6 octahedra which share corners. Alkali metal ions (M) are denoted by dots which reside in the hexagonal cages (After Kihlberg 1983). For $\text{Rb}_{0.27}\text{WO}_3$, the lattice constants are $a = 7.38$ Å, $c = 7.56$ Å with space group $D_{6h}^3 - c6/mcm$ (Magneli 1953).

3. The role of J-T effect on the electronic structure and phase transitions

Some authors (Stanley *et al* 1979; Cadwell *et al* 1981) believed that alkali metal ions are mainly responsible for the anomalous electronic properties of these systems. Indeed, the idea was mooted whether the transition of the high temperature uncorrelated to low temperature correlated motion of alkali metal ions in the hexagonal channels might provide a possible mechanism. Along this theme a few workers (Ngai and Reinecke 1978; Vujicic *et al* 1981) had invoked interaction between electrons and local structural excitations in the phase transition regions. This new interaction will give an additional superconductivity pairing mechanism. But this mechanism can be important only when the temperature of the structural phase transition T_s is close to the superconducting transition temperature T_c .

We have seen earlier that for $M_x\text{WO}_3$ systems, the structural transition temperatures T_s and T_c are several hundred degrees above T_c which is less than 8 K. It is extremely unlikely that local structural excitations will exist at low temperature (< 10 K). Accordingly, this mechanism can be ruled out for giving anomalous superconducting behaviour. At such low temperatures, the ordering of alkali atoms has already taken place.

The observed softening of the optical phonon mode at the Γ point is much more relevant in that it is related to the distortion of the WO_6 octahedra. However, the corresponding transition temperature T_R (~ 420 K) is again hundred times higher than T_c . Its influence will come through the modulation of electronic density of states because of distortion (induced by J-T effect). To summarize, the central point of our approach is to examine the effect of the concentration-driven structural transition which has already taken place at high temperature on the electronic structure of the systems in question in the low temperature region (< 10 K).

In HTB systems, we have formations of chains of WO_6 octahedra along the c -axis and in the basal plane along three directions which are related to each other by rotation (around the c axis) by 120° . The alkali metal atoms, having donated their valence electron, are in the closed shell configuration. These ions also form linear chain but there will be interruptions when their concentration falls below $x = 0.33$. Their role in the electronic structure of the system is secondary. They may provide Einstein-type modes of vibration (Kamitakahara *et al* 1979) and their ordering will have some effect on the distortion of the lattice. Thus the conduction mechanism and the electronic band structure stem primarily from the WO_6 octahedral chains along the four directions mentioned above. The electronic configuration of atomic tungsten W is (closed shell + $5d^4 6s^2$). In WO_3 , the ionic configuration is $\text{W}^{6+} \text{O}_3^{2-}$, i.e. W ion has lost all its valence electrons. Indeed solid WO_3 is an insulator and there are no free electrons in the conduction band. The conductivity and superconductivity of $M_x\text{WO}_3$ arise from the electrons (one each from each M atom) donated by the alkali atoms to tungsten $5d$ states. In the field of the 6O^{2-} ions in WO_6 octahedron, the three t_{2g} orbitals of the W

SrTiO₃ (Shukla and Sinha 1966). We believe that the role of J-T effect will be more pronounced in M_xWO₃ system, than Nb₃Sn or V₃Si (as invoked by Labbe and Friedel 1966) owing to a larger electromagnetivity of the oxygen than Sn or Si. In the light of the above, we propose that at and beyond a critical concentration x of M atoms in M_xWO₃, there is cooperative J-T effect which will lead to structural phase transition due to in-phase distortion of octahedra. For incomplete cooperativity, there may be only local distortion at various octahedra. As a consequence of these transitions, we expect splitting or shifting of the lowest conduction band.

The electrons in the HTB are to be treated as J-T polarons (Shukla and Sinha 1966; Höck *et al* 1983). For the electrons moving in the octahedral chains, there are two competing mechanisms. These are the delocalizing effect of the intersite hopping and the localizing effect of the J-T induced electron-phonon coupling.

The Hamiltonian for such a system is

$$H = H_{el} + H_L + H_{J-T}, \quad (1)$$

where H_{el} is the electronic Hamiltonian having the form

$$H_{el} = \sum_{m\sigma} \varepsilon_m^0 C_{m\sigma}^+ C_{m\sigma} + \sum_{m \neq n, \alpha\alpha'} t_{mn}^{\alpha\alpha'} (C_{m\sigma}^+ C_{n\alpha'\sigma} + \text{h.c.}), \quad (2)$$

the Jahn-Teller term

$$H_{J-T} = -A \sum_{m\sigma} Q_m (C_{m1\sigma}^+ C_{m1\sigma} - C_{m2\sigma}^+ C_{m2\sigma}), \quad (3)$$

and H_L denotes the lattice Hamiltonian which includes the coupling between the J-T active vibrational coordinates between different sites. Here $C_{m\sigma}^+$ ($C_{m\sigma}$) represents creation (annihilation) operators for electrons of spin σ in a Wannier state at site m and in the doubly-degenerate orbital ϕ_α ($\alpha = 1, 2$); Q_m refers to the local (symmetry-breaking) J-T active vibrational coordinate. A is the coupling coefficient.

When this coordinate takes a value $\langle Q_m \rangle$, which is non-zero, the term H_{J-T} leads to a local distortion around the electron. In fact H_{J-T} then provides an effective potential. For strong coupling A , the electron may become trapped and the composite J-T polaron moves as a new entity through the lattice of WO₆ chains. Thus depending on the strength of A the electronic motion may vary from a diffusive motion to a coherent band motion.

In the present paper, we shall not discuss the quantitative aspects of the J-T polarons in HTB systems. Instead, we shall examine the features of the band structure of HTB in the undistorted phase and then draw qualitative conclusion of the changes that can arise on taking into account the J-T mechanism.

The orientations of the two degenerate orbitals dxz , dyz of each W ions in the HTB structure is such that there is greater overlap between identical orbitals along the c -direction than overlap between two different orbitals of W atoms in the basal plane. Accordingly, we expect a larger hopping integral along the c -direction than in the basal plane where each tungsten is surrounded by three equivalent neighbouring tungsten sites.

Tight-binding approximation with nearest neighbour W-W interaction gives the

dispersion relation

$$E(\mathbf{k}) = E_0 - 2t_1 \cos \frac{a}{4}(k_x - \sqrt{3}k_y) - 2t_2 \cos \frac{a}{4}(k_x + \sqrt{3}k_y) \\ - 2t_3 \cos \frac{a}{2}(k_x) - 2t_0 \cos \frac{c}{2}k_z, \quad (4)$$

where a and c are lattice constants defining the unit cell, (k_x, k_y, k_z) are wave vectors in the cartesian directions and t_0, t_1, t_2, t_3 are the magnitudes of the transfer integrals along the c -axis and the three directions along the WO_6 chains in the basal plane respectively. For the undistorted situation we have $t_1 = t_2 = t_3$ and the above dispersion relation is invariant under rotation by $n\pi/3$, (n integer) around the c -axis. We believe the minimum of the band structure lies at the Γ point *i.e.* $(0, 0, 0)$ of the Brillouin zone (BZ). Further t_0 is much larger than t_1 etc owing to large end on overlap of the orbital functions along the c -axis than those in the basal plane. Accordingly, we expect a narrow band in the hexagonal plane of the BZ. We shall not go into the details of the band structure and the concomitant density of states as it will be discussed elsewhere (Ranninger and Sinha 1985). We shall summarise the salient features.

For small wave vectors the dispersion in the basal plane is isotropic but with its increasing magnitude the Fermi surface approaches a hexagonal shape. Near the zone boundary the anisotropy in the dispersion becomes very dramatic. Along the k_x direction the electron energy drops monotonically to zero. On the otherhand in the k_y direction it increases slightly, goes through a maximum and then approaches the BZ in a fairly flat manner.

There is a logarithmic singularity in the density of states arising from the flat portion of the electron dispersion for wave vectors $k_\rho \sim k_\rho^0$ at the zone boundary (note the dispersion was written in cylindrical coordinates, $k_x = k_\rho \cos \phi$, $k_y = k_\rho \sin \phi$). A small anisotropy in the dispersion will wash out this singularity giving rise to a narrow peak centred around the energy value

$$\varepsilon_0 = Bk_\rho^{0^2}/2, \quad B \text{ being a constant.}$$

The electronic density of states increases as $\varepsilon^{1/2}$ for small energies but above ε_0 it decreases as $1/\varepsilon^{1/2}$. The reason is that the dispersion in the basal plane is rather flat compared to the dispersion along the c -direction.

For small values of the energy ε we have a dispersion of the form $\varepsilon_k \propto t_0 k_z^2 + t_1 k_x^2$, and hence the density of states is proportional to $\varepsilon^{1/2}$. When ε is around ε_0 all the states in the basal plane have been filled. Beyond this only states with k -vectors in the c direction are available. In this range the system would reflect a quasi one-dimensional density of states which will fall off as $1/\varepsilon^{1/2}$.

Let us now consider the effect of the phase transition as the concentration of alkali metal ion varies. In effect, this leads to the change in the number of electrons in the WO_6 chains. The phase transition involves mainly the distortion of the octahedra and the order of M atom. As remarked earlier, in our view, it is the first which produces the dominant effect on the dispersion relation and the density of states. The distortion will alter the values of the hopping integrals which will lead to a shift of the bottom of the band and the density of states curve may expand or contract (depending on the

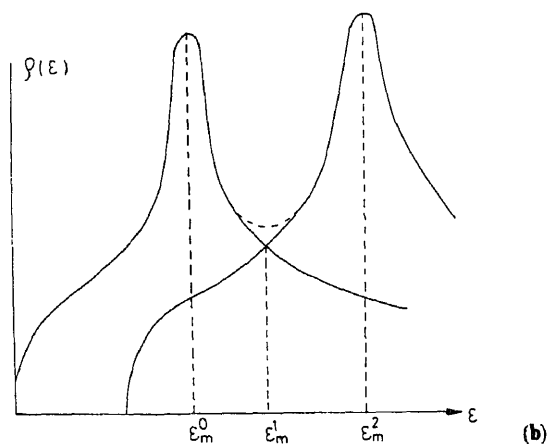
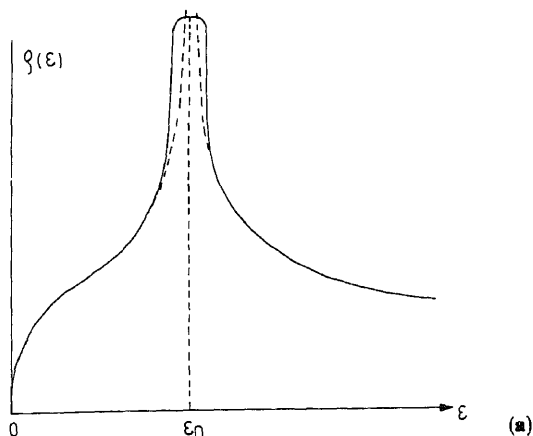


Figure 2a. Density of states $\rho(\varepsilon)$ as a function of ε for HTB in the undistorted phase (dashed curve). The solid line gives the situation after smoothening the peaks due to distortion.

Figure 2b. Density of state profile for HTB undergoing a cooperative J-T effect above a critical concentration x_c . A superposition of two density of states profile of the type given in figure 2a before and after the structural transition. The rounding off (dashed portion) is expected for realistic density of states.

2b. When the two situations are taken together, a realistic density of states profile will have the following behaviour as a function of x . It will have one pronounced hump followed by a minimum and then rise again to a second hump. The precise form of this behaviour will depend strongly on the size of the substituted alkali metal ions.

4. Superconducting transition temperature

Now as a function x (hence electron concentration) the Fermi level will explore different regions of the density of states ($\rho(\epsilon)$) profile. Our stipulation is that the anomalous behaviour in these HTB system arises from the fact that the Fermi level lies around the peak portion of $\rho(\epsilon)$. Since the peaks are smoothened (see § 3), we can parametrize the relevant part of $\rho(\epsilon)$ as a series of three parabolic sections, corresponding to a maximum at an energy $\epsilon_m^{(0)}$, followed by a minimum at $\epsilon_m^{(1)}$ and a maximum at $\epsilon_m^{(2)}$ (figure 2b). Thus we can write

$$\rho(\epsilon) \approx A_l - (-1)^l B_l (\epsilon - \epsilon_m^{(l)}), (l = 0, 1, 2). \quad (5)$$

where A_l and B_l are coefficients. We expect that the position of maxima increases as we go from Cs $\rightarrow$ Rb $\rightarrow$ K. We intend to fit the T_c dependence on the electron concentration of these three HTB on the basis of the corresponding variation of density of states at the Fermi level. Accordingly, we have to express the dependence of $\rho(\epsilon)$ on x , the electron concentration. We have

$$\begin{aligned} x &= \int_0^{\epsilon_F} d\epsilon \rho(\epsilon) = \int_0^{\epsilon_m^{(l)} + (\epsilon_F - \epsilon_m^{(l)})} d\epsilon \rho(\epsilon) \\ &\approx \int_0^{\epsilon_m^{(l)}} d\epsilon \rho(\epsilon) + (\epsilon_F - \epsilon_m^{(l)}) \rho(\epsilon_m^{(l)}) \\ &= x_m^{(l)} + (\epsilon_F - \epsilon_m^{(l)}) \rho(\epsilon_m^{(l)}); \end{aligned} \quad (6)$$

where $x_m^{(l)}$ corresponds to $\epsilon_m^{(l)}$ and ϵ_F is the Fermi energy. Thus

$$\begin{aligned} \rho(\epsilon_F) &\approx \rho(\epsilon_m^{(l)}) - (-1)^l \frac{1}{2} (\epsilon_F - \epsilon_m^{(l)})^2 \rho''(\epsilon_m^{(l)}) \\ &= \rho(\epsilon_m^{(l)}) - (-1)^l \frac{1}{2} \left(\frac{\rho''(\epsilon_m^{(l)})}{\rho^2(\epsilon_m^{(l)})} \right) (x - x_m^{(l)})^2. \end{aligned} \quad (7)$$

The expression of the transition temperature T_c (see Sinha 1978) is

$$T_c = W_c \exp[-1/\lambda_{\text{eff}}], \quad (8)$$

where W_c is the energy cut-off in temperature units and

$$\lambda_{\text{eff}} = \rho(\epsilon_F) V, \quad (9)$$

being the effective electron-electron interaction constant. Our assertion is that the changes in density of states (which is split due to phase transition driven by concentration-dependent cooperative J-T effect) determines the behaviour of T_c in these systems, with V showing no appreciable change. Thus we reexpress λ_{eff} as

$$\lambda_{\text{eff}} = [\alpha_l - (-1)^l \beta_l (X - X_m^{(l)})^2], \quad (10)$$

where the coefficients have absorbed the interaction constant V also; hence α_l, β_l are dimensionless numbers. Using expressions (8) and (10) we have calculated the transition temperature T_c by evaluating the parameters α_l and β_l for the positions of the extrema in $X_m^{(l)}$. The calculated T_c along with the experimental results are shown in figure 3. For K_xWO_3 the splitting *i.e.* spacing between the two peaks in $\rho(\epsilon)$ is maximal.

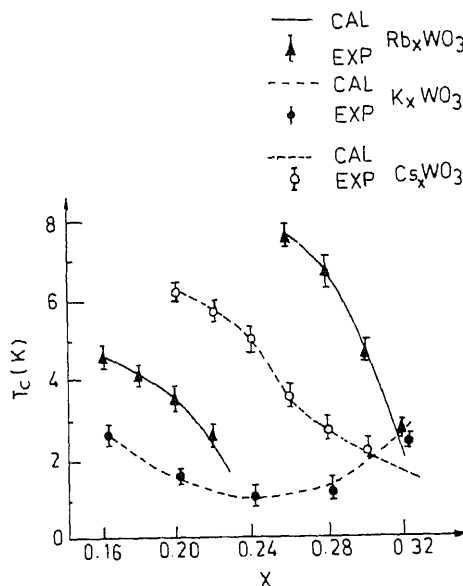


Figure 3. Superconducting transition temperature T_c as a function of concentration x for $M_x\text{WO}_3$. The parameters for calculation are

K_xWO_3 : $W_c = 150$ K, $\alpha_m^{(1)} = 0.20$, $\beta_m^{(1)} = 7.15$, $x_m^{(1)} = 0.24$.

Rb_xWO_3 : $W_c = 115$ K, $\alpha_m^0 = 0.3086$, $\beta_m^0 = 13.875$, $x_m^0 = 0.16$, $\alpha_m^{(2)} = 0.3663$, $\beta_m^{(2)} = 11.5$, $x_m^{(2)} = 0.26$.

Cs_xWO_3 : $W_c = 170$ K, $\alpha_m^0 = 0.3020$, $\beta_m^0 = 11.5$, $x_m^0 = 0.20$, $\alpha_m^{(1)} = 0.22$, $\beta_m^{(1)} = 7.25$; $x_m^{(1)} = 0.24$.

The relevant portion of $\rho(\epsilon)$ being essentially between the two maxima. For Rb_xWO_3 the two maxima lie fairly close together—the region of the minimum being too small for the transition being sharp. For Cs_xWO_3 the band splitting is undetectably small. The density of states are parametrized by a parabolic maximum decreasing towards a distant minimum. The agreement between calculated curves and the observed T_c as a function of x is reasonably good.

5. Concluding remarks

The foregoing analysis of the experimental results and the proposed model for $M_x\text{WO}_3$ systems suggest the following picture.

The concentration of conduction electrons in $M_x\text{WO}_3$ can be varied over a wide range by doping with alkali metal atoms (M). The principal role of these atoms is to donate their valence electrons to the WO_3 network which provides the conduction channels. Owing to doubly degenerate orbital states of these donated conduction electrons in WO_6 octahedra, they are subject to a J-T distortion. This leads to a cooperative above a critical concentration x_c (~ 0.24) of M atoms leading to a structural phase transition. This is indeed supported by neutron scattering experiments.

by distortion of octahedra) occur at temperatures very much higher than the superconducting transition temperature. Thus the mechanism based on local structural excitations (Vujicic *et al* 1981) cannot hold good as these are frozen out. The J-T induced distortions do, however, provide a self-consistent potential in which the electrons move. The situation is akin to a polaron. In the present case we are dealing with a J-T polaron which is associated with a symmetry-breaking vibrational mode of the complex (Shukla and Sinha 1966; Höck *et al* 1983). When cooperativity is complete above a critical concentration, there is a phase transition which leads to a splitting and shifting of the density of states profiles. When cooperativity is incomplete there will exist local distortions of octahedra. Such random local distortions will smear the peaks in the density of states. The model of the density of states suggested here also provides an explanation of the anomalous transport properties details of which will be given elsewhere (Ranninger and Sinha 1985).

Now a few words about the important modulating role of the density of states at the Fermi level on the superconducting transition temperature. The explicit expression for λ_{eff} is given by

$$\lambda_{\text{eff}} = \frac{\rho(\varepsilon_F) \langle I^2 \rangle}{M_{\text{eff}} \langle \omega^2 \rangle},$$

where $\langle I^2 \rangle$ is the average electron-phonon matrix element taken over the Fermi surface, $\langle \omega^2 \rangle$ is the average phonon frequency squared and M_{eff} is the effective mass of the ions in the complex. The renormalized Coulomb interaction μ^* between electrons is negligible in these systems. Varma and Dynes (1976) have demonstrated that in a given category of materials and for the same type of d orbitals involved near the Fermi surface, the quantity $\langle I^2 \rangle / M_{\text{eff}} \langle \omega^2 \rangle$ is approximately constant. Thus the variation of the quantity λ_{eff} in this class of materials is determined exclusively by the density of states at the Fermi level. Our analysis of HTB system supports this correlation between λ_{eff} and $\rho(\varepsilon_F)$.

Finally, it should be mentioned that we have taken the situation wherein the conduction band is derived from the antibonding combination of tungsten t_{2g} orbitals and oxygen p_π orbitals. On a J-T induced phase transition the density of states for antibonding states will be pushed up along with a decrease of lattice energy due to distortion involving symmetry-breaking modes which may include anharmonic terms in the quasielastic restoring forces (Pryce *et al* 1965). This leads to an overall lowering of energy after the structural phase transition.

For bonding states density of states would go in the opposite direction. It is desirable to make a detailed band structure calculation invoking (d) orbitals of W atoms and (p) orbitals of the oxygen atoms and determine the detailed nature of the electronic band structure and the corresponding density of states. We believe the shifting and splitting of density of states peaks on phase transition (whether going up or down) explains the behaviour of the superconducting transition temperature. The relevant parameters have to be determined for each situation.

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magnetic probes in membrane biophysics

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Abstract. The use of paramagnetic probes in membrane research is reviewed. Electron paramagnetic resonance studies on model and biological membranes doped with covalent and non-covalent spin-labels have been discussed with special emphasis on the methodology and the type of information obtainable on several important phenomena like membrane fluidity, lipid flip-flop, lateral diffusion of lipids, lipid phase separation, lipid bilayer phase transitions, lipid-protein interactions and membrane permeability. Nuclear magnetic resonance spectroscopy has also been effectively used to study the conformations of cation mediators across membranes and to analyse in detail the transmembrane ionic motions at the mechanistic level.

Keywords. Membranes; electron paramagnetic resonance; nuclear magnetic resonance; spin-labels; paramagnetic probes.

ction

n of living matter in cells is crucial for the sustenance of living beings. are primarily responsible for this organization giving rise to distinct known as cells, mitochondria, ribosomes, nuclei etc. In addition to this ntalization, several cellular functions such as endocytosis, exocytosis, munication, nerve-cell excitation, fertilization etc involve membranes in the other. The chemical basis for the function of membranes lies in the e nature of lipids, which form the backbone of membrane structure. biological membranes are made up of mostly proteins in addition to lipids. e nature of these proteins, called membrane proteins, is different from that er functional proteins. Membrane proteins are known to adopt conform- n are largely helical and to have hydrophobic exteriors.

ly, understanding the membrane structure has been mainly aided by model systems (Fendler 1982) like the monolayers at the air-water interfaces s formed by surfactants and recently the lipid vesicles or liposomes. chemistry has revealed the tendency of the amphipathic surfactants, s and lipids to form aggregates. The hydrocarbon chains of these come together, away from water, so as to form oily microenvironments he so-called hydrophobic effect (Tanford 1973). Whereas certain amphi- ost of the surfactants and lysolecithins form either monolayers or micelles, chain lipids form inhomogeneous aqueous suspensions. These structures ellar in morphology with an onion-like arrangement of several bilayers ck up on the application of ultrasonic irradiation to form small, closed ed unilamellar vesicles (Bangham 1968). The micelles, reverse micelles, and multilamellar vesicles are schematically represented in figure 1. ent of proteins in a lipid bilayer matrix is the significant feature of the cepted model for membranes (Singer and Nicolson 1972). In this model, either incorporated into the lipid bilayer (integral proteins) or mostly lie on

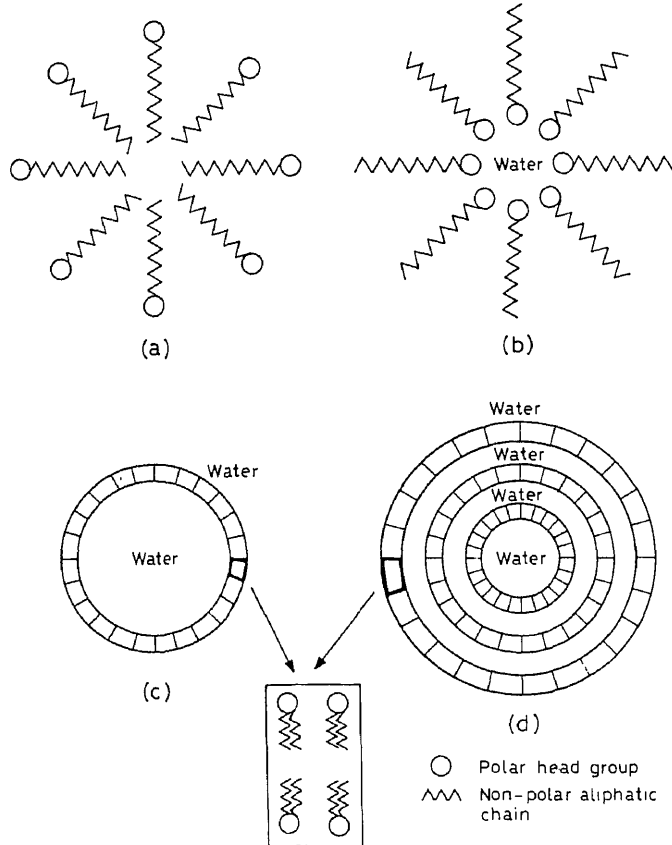


Figure 1. Schematic representation of (a) micelles, (b) inverted micelles, (c) unilamellar vesicles and (d) multilamellar vesicles.

the surface of it (peripheral proteins). Molecules freely diffuse laterally in the plane of the membrane.

Contemporary research in membrane biophysics is largely concerned with head group conformation, membrane fluidity, mechanisms of membrane transport, conformations of ionophores and membrane proteins, lipid-protein interactions, lateral and transverse diffusion of lipids in membranes and phase separation and domain formation. Electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectroscopic techniques have helped to understand these aspects of membrane structure and function in a fairly good detail. In this review, we will describe the use of paramagnetic probes in EPR and NMR to understand the membrane structure and function.

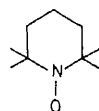
In general, biological membranes contain no paramagnetic centres. The introduction of a paramagnetic label enables one to use EPR spectroscopy to probe into membrane structure and dynamics. Spin-labels and paramagnetic cations have been very effectively used towards this end. All the spin-labels used so far are nitroxide free radicals and are either covalently linked to the lipids and membrane-active systems or

2. Spin-labels

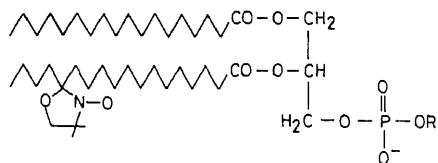
Most of the spin-labels are derived from the oxazolidine and the piperidine or pyrrolidine rings (Rozantsev 1970) with the nitroxide group flanked by quaternary carbon atoms. Chemical structures of some spin-labels are shown in figure 2. The EPR spectra of these spin-labels (Berliner 1976) exhibit a three-line nitrogen hyperfine structure. The hyperfine splitting is dependent on the orientation of the magnetic field with respect to the nitroxide axes. When the motion of the spin-labels is fast compared with the spectral anisotropies, a three-line spectrum with equal line heights would be obtained. This corresponds to an isotropic correlation of time of 10^{-11} sec. As the motion becomes slow, there will be a differential broadening of the spectrum, with the line position unchanged. For still slower motions, the line positions and shapes get distorted. At the extreme end of complete immobilization, the so-called powder pattern is observed. In the case of fast but anisotropic motion, the spectral anisotropy is only partially averaged. In this case, the degree of motional averaging is a measure of the angular amplitude of anisotropic motion. These angular amplitudes are described in terms of order parameters. An order parameter of zero corresponds to an isotropic situation and it approaches unity with decreasing rates of motion.

3. Membrane fluidity

The nitroxide moiety can be covalently attached to the lipid, proteins and steroids. Several spin-labelled lipids and fatty acids have been synthesized with the label attached to the head group and at various carbon atoms of the hydrocarbon (Marsh 1981a). EPR

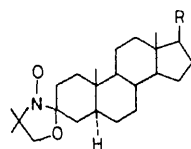


(a)



R = H Phosphatidic acid
 R = $(\text{CH}_2)_2\text{-NH}_3^+$ Phosphatidyl ethanol amine
 R = $(\text{CH}_2)_2\text{-N}(\text{CH}_3)_3$ Phosphatidyl choline
 R = $\text{CH}_2\text{-CH(NH}_3^+\text{)-COO}^-$ Phosphatidyl serine
 R = $\text{CH}_2\text{-CHOH-CH}_2\text{OH}$ Phosphatidyl glycerol

(b)



R = Cholestane
 R = -OH Androstanol
 R = -H Androstane

(c)

phatidylcholine spin-labels with the labels progressively going down the acyl chain have shown that the anisotropy of the spectrum, and hence the order parameter, decreases (Knowles *et al* 1976). This means that the motion increases as one goes from the head group to the interior, suggesting the existence of a flexibility gradient. The flexibility gradient arises because the lipid chains are anchored at the glycerol backbone of the lipid and the number of carbon-carbon single bonds that can undergo trans to gauche conversions increases down the chain (Marsh 1974). Several models have been proposed considering the interdependence of rotation about adjacent C-C single bonds (Seelig 1971), probabilities of trans to gauche conformers (Hubbell and McConnell 1971), intermolecular steric restrictions on the chain conformations (Marsh 1974) and interchain interactions (Marcelja 1974; Schindler and Seelig 1975) to account for the observed flexibility gradients and to calculate order parameters, probabilities of trans and gauche conformers, rotation potentials and several structural and thermodynamic properties.

Although EPR studies using spin-labelled lipids have provided a wealth of information, the perturbing effect of the nitroxide label group on the labelled chain and the surroundings has been considered a drawback. It has been argued that ^2H NMR provides a better source of information because ^2H is a non-perturbing probe (Schindler and Seelig 1975; Marsh 1981b).

4. Lateral diffusion

Lipid molecules freely diffuse laterally in the plane of the membrane. The rate of lateral diffusion is directly proportional to the collision frequency of two lipid molecules. When they are tagged by a spin-label, the inter-spin-label interactions would provide a measure of the lateral diffusion coefficients. For these experiments, concentrations of spin-labels used are normally higher than those used for other studies. At these concentrations, the spin-label-spin-label exchange interaction becomes appreciable leading to measurable interaction broadening. The dipolar and exchange contributions to the interaction broadening can be distinguished by line shape simulation and temperature dependence. Broadening could arise due to diffusion-controlled interactions or by label segregation. These two processes are easily distinguished by their different concentration dependence. Methods have been developed considering the process as a two-dimensional, homogeneous diffusion (Trauble and Sackmann 1972) or an exchange between nearest neighbours on a hexagonal lattice (Devaux *et al* 1973) to calculate diffusion coefficients from collision frequency. Lateral diffusion coefficients have been calculated for steroid spin-label in dipalmitoylphosphatidylcholine (DPPC) bilayers to be $10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ (Trauble and Sackmann 1972) and for a phosphatidylcholine spin-label in sarcoplasmic reticulum membrane vesicles to be $6 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ (Scandells *et al* 1972).

5. Lipid flip-flop

The transverse motion of lipids or a flip-flop of the lipid molecules between the two halves of the bilayer is much slower than the lateral diffusion rate accounting for the structural stability of a bilayer. This also leads to an asymmetric distribution of lipids

of ascorbate at 0°C to a head group spin-labelled lipid containing vesicles. Ascorbate reduces the head group spin-labels on the outer half.

The intensities of the EPR lines before and after ascorbate reduction are proportional to the total lipid and lipid in the outer half respectively and hence can be used to calculate the fraction of lipids in the inner half. Values in the range of 0.25–0.35 are normally obtained for small sonicated vesicles and about 0.5 for large vesicles (Kornberg and McConnell 1971). Immediately after the ascorbate reduction, it can be eluted and the rate of flip-flop easily measured. The lipid flip-flop is considered a reversible, pseudo-unimolecular process. Experiments on egg phosphatidylcholine vesicles showed that the asymmetry decayed with a half-time of 6.5 hr, with probabilities of 0.07/hr and 0.04/hr for the outward and inward migrations. On the other hand, much faster rates (half-time 4–7 min) are observed for the excitable membrane vesicles from the electroplax of *Electrophorus electrons* (McNames and McConnell 1973).

6. Lipid phase separation

Certain lipid mixtures form bilayer structures but do not mix homogeneously. In this case, the measured exchange interaction can be used to analyse the lipid segregation in terms of the cluster size and density. Using a steroid spin-label, in DPPC bilayers below the phase transition temperature, a cluster density of $3.4 \times 10^{11} \text{ cm}^{-2}$ and an increase in the number of molecules per cluster from 25 to 150 with increasing concentration have been obtained (Trauble and Sackmann 1972). It was shown that PC and dipalmitoyl-phosphatidic acid (DPPA) phase separate in the presence of Ca^{2+} with a cluster density of $3.2 \times 10^{11} \text{ cm}^{-2}$ (Galla and Sackmann 1975).

Phase separation is easily detected using non-covalent labels which partition into a fluid membrane and practically do not enter a rigid interior. The free-radical 2,2,6,6-tetramethyl piperidin-1-oxyl (TEMPO) has been widely used to demonstrate solid phase and fluid phase immiscibilities (Shimshick and McConnell 1973).

7. Lipid bilayer phase transitions

Many aqueous dispersions of saturated lipids have a temperature below which the hydrocarbon chains are rigid. At a given temperature known as the phase transition temperature, the chains melt resulting in a cooperative phase transition from a gel to a liquid crystalline phase (Mabrey and Sturtevant 1978). This transition is accompanied by a sharp rise in the gauche conformers making the hydrocarbon interior fluid. Spin-labels like TEMPO are partitioned into the bilayer more when the bilayer is in the liquid crystalline phase than in the gel phase. EPR spectrum of TEMPO in hydrocarbons is different from that in water. This allows one to measure the uptake of TEMPO into the bilayer from the line heights and hence the phase transition temperature (Shimshick and McConnell 1973). The temperature dependent EPR spectra in DPPC multibilayers is shown in figure 3. Values obtained thereby are considered, on the one hand, to be in good agreement with those from differential scanning calorimetry but the differences also have been attributed to the perturbing effect of TEMPO and its specificity in interaction with the bilayer making it a less efficient probe.

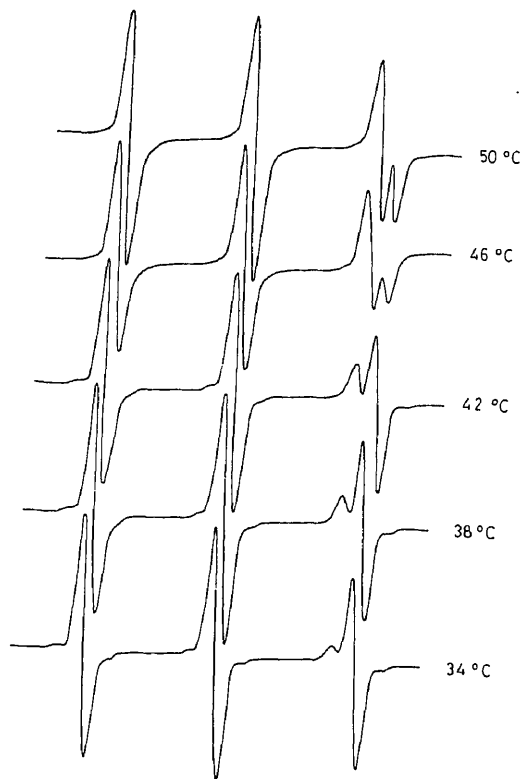


Figure 3. Electron paramagnetic spectra of TEMPO in DPPC multibilayers as a function of temperature (DPPC) = 0.18 M (TEMPO) = 0.75 mM phase.

Effects of additives on the phase transition have been studied using TEMPO partitioning EPR (Watts *et al* 1978). We have studied the lipid bilayer phase transition temperature of DPPC bilayers upon incorporation of the ionophore, valinomycin (Sankaram and Easwaran 1984). The phase transition temperature was unchanged upon addition of valinomycin but the pre-transition has been broadened (figure 4). These observations were attributed to a preferential location of the ionophore near the head group region. As the concentration of added valinomycin was increased, a decrease was observed in the uptake of TEMPO into the bilayer above the transition temperature ruling out any specific spin-label ionophore interactions. It appears that this is due to sharing of the available interior volume by both valinomycin and TEMPO (Sankaram 1983).

8. Lipid-protein interactions

Effects of membrane proteins on the organization of lipids in membranes have been successfully studied using spin-labelled lipids. Information on the stoichiometries of the lipid-protein complexes, specificity of lipid-protein interactions and the orders of selectivity has been obtained on several membrane proteins.

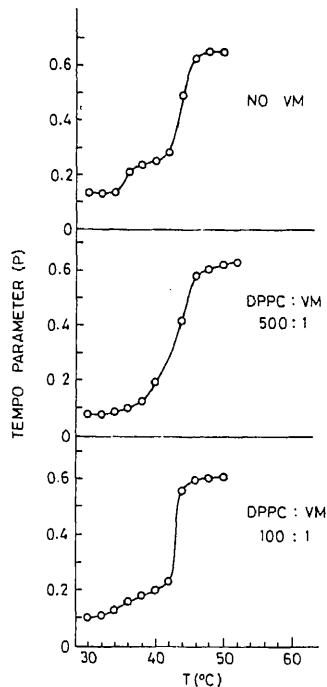


Figure 4. Transition temperatures of DPPC-VM multibilayers by spin-label partitioning EPR (DPPC) = 0.18 M (TEMPO) = 0.75 mM.

Lipids labelled both at the head group and the hydrocarbon chains have been employed. The modes of interaction between the integral and peripheral membrane proteins have been found to be characteristic of their structures. The overall picture of a protein in a lipid environment is that of a motionally restricted component of the lipids around the protein with the local ordering decreasing as one goes away from the protein.

Membrane proteins can also be spin-labelled at the sulphhydryl groups which can be alkylated by maleimide and iodoacetamide nitroxide derivatives. EPR spectra of spin-labels covalently bound to the proteins in chromaffin granule membranes show strongly immobilized and small mobile components superimposed (Marsh *et al* 1976). The covalent protein labels have also been used to detect ligand-induced conformational changes in membrane-bound enzymes, receptors and transport proteins like Ca^{2+} -transporting ATPase of sarcoplasmic reticulum (Marsh 1981b).

9. Membrane permeability

The ascorbate reduction used in the lipid flip-flop studies can also be used for studying membrane permeabilities. In this case, the spin-label is added to the aqueous media and its permeability is measured. Permeability of TEMPO choline across DMPC bilayers has been measured in this way (Marsh *et al* 1976b). Trapped volumes of vesicles, vesicle permeability coefficients, diffusion coefficients and membrane potentials can be

namely the mediated cation transport can be conveniently studied using hydrophilic, paramagnetic probes in NMR.

Transmembrane cation transport is mediated by ionophores, membrane proteins and possibly by acidic phospholipids. The mechanisms of their action are classified as the diffusive carrier, relay carrier, channel and pore mechanisms which are illustrated in figure 5. The actual transport mechanism of a given system would be an appropriate admixture of these idealized cases. The diffusive carriers complex with the cation at one of the membrane-water interfaces and carry the cation to the other side by diffusion. The relay carrier mechanism involves, in addition to a diffusion of the carrier-cation complex, a handing over of the cation from one ionophore to the other. The carrier type ionophores valinomycin, nonactin, lasalocid, A23187 etc. act by these mechanisms (Ovchinnikov *et al* 1974). These ionophores complex with the cations to form equimolar and ion-sandwich complexes (Easwaran 1985; Vishwanath and Easwaran 1981, 1982, 1984; Shastri and Easwaran 1984). On the other hand, the channel and pore forming molecules bind to cations less strongly. They provide a hydrophilic interior which cations can pass through. Channels open randomly and per opening permit a given number of cations inside. A few such openings will saturate the inner pools. Pores allow a maximum number of cations sufficient to saturate the inner pools per opening.

Recent developments in the use of hydrophilic probes like lanthanides have permitted the use of NMR to study transmembrane ionic motions. Lanthanides when added to one side of the vesicle either shift the signals from the head group (phosphate and choline) on that side either upfield or downfield depending on the nature of the lanthanide or broaden them (Bystrov *et al* 1971). The effect of lanthanides on the ^1H NMR spectra of vesicles is shown in figure 6. Addition of a cation mediator to the vesicle sample containing the lanthanide on one side leads to a time-dependent increase in the intravesicular lanthanide ion concentration. Correspondingly, the NMR signals from the inside change their chemical shift, linewidth and intensity with time to approach the signals from the outside. The processes taking place during transport are shown in figure 7. The information on the mechanism of transport is contained in these changes (Ting *et al* 1981).

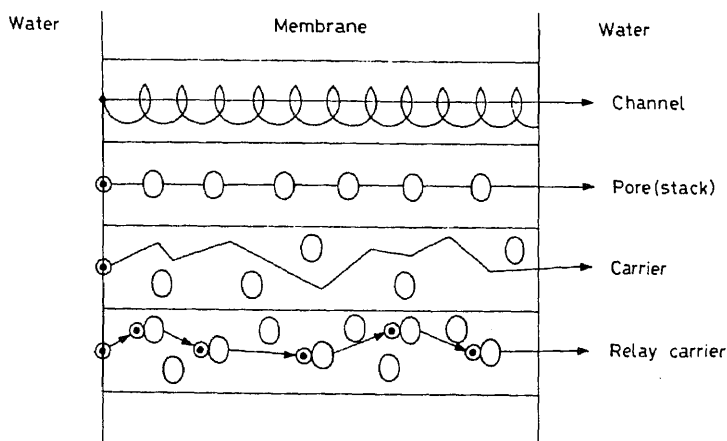


Figure 5. Mechanism of cation transport.

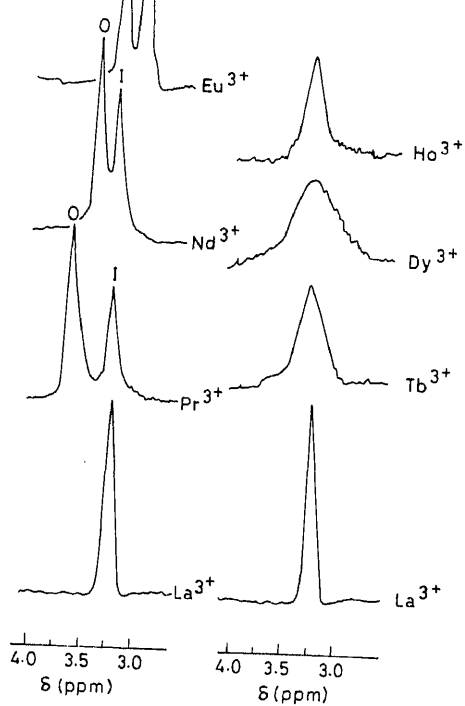


Figure 6. Effect of lanthanide addition on the ^1H NMR spectra of DMPC vesicles at 30°C .

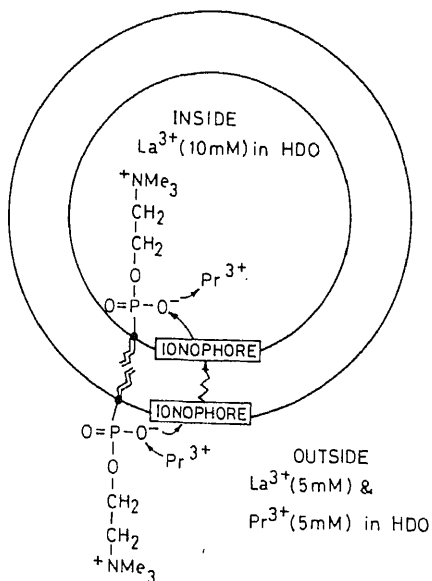
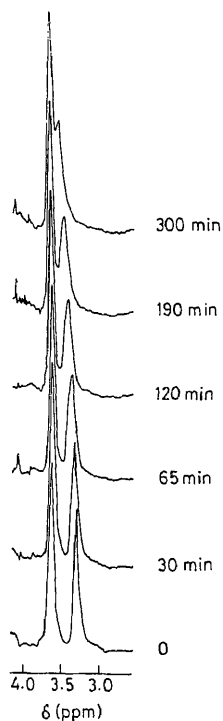


Figure 7. Strategy of the NMR kinetics experiments.

Using these methods, it has been shown that the carboxylic acid ionophores; lasalocid, A23187, etheromycin, tetronomycin, M139603, X-14547A and narasin (see Sankaram and Easwaran 1985a, b; Grandjean and Laszlo 1983) act by a diffusive carrier mechanism. These ionophores have been shown to transport Pr^{3+} orders of magnitude faster than the neutral class of ionophores due to the inability of proton antiport by the latter class. When two carboxylic ionophores are added together, they transport Pr^{3+} synergistically i.e. by a positive cooperative effect. Proton NMR spectral changes for the A23187 induced Pr^{3+} transport are shown in figure 8.

Lysolecithins and certain surfactants like triton X-100, bile salts form tetrameric structures to transport Pr^{3+} by an essentially diffusive mechanism. These tetrameric aggregates have been proposed to be reverse micellar in structures. Departures from transporting activity leading to perturbations in the membrane structure have been noticed in certain cases.

Pumping of cations in bursts, either a sufficient number per one opening or less, is manifested by a growth of new peaks in the NMR spectra without any chemical shift changes in the outer and inner signals. Growth of peaks corresponding to several partially filled inner pools at the expense of the inner choline signals has been observed for channels and pores. This kind of behaviour is exhibited for light induced Eu^{3+} transport by rhodopsin (O'Brien *et al* 1977) thermally-induced Eu^{3+} and Nd^{3+} permeation (Ting *et al* 1981) sonication-induced Pr^{3+} and Eu^{3+} permeation (Ting *et al* 1981) and cardiolipin-induced Pr^{3+} translocation (Sankaram *et al* 1985a). We have identified a borderline situation where the kinetics are carrier-like but the transporting



activity is a hexameric pore in the case of synthetic cyclo (L-Pro-gly)₃ mediated Pr^{3+} transport (Sankaram 1983).

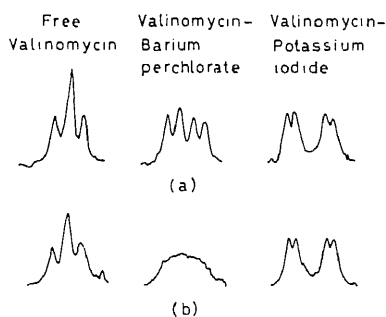
10. Conformations of ionophores

Conformations of ionophores in solution are studied in detail by NMR spectroscopy. Paramagnetic probes have been used to delineate the intramolecular hydrogen bonding in peptide ionophores and to study the conformations of the cation complexes. Thus, the spin-label TEMPO has been used with success to detect the presence of intramolecular hydrogen bonds (Wuthrich 1976) in ion-binding cyclic peptides like valinomycin (Devarajan and Easwaran 1984). Presence of such a hydrogen bond leads to an absence of broadening of the amide protons upon addition of the spin-label and an appreciable broadening of the exposed amide protons. Use of TEMPO to delineate the hydrogen bonding in valinomycin and its K^+ and Ba^{2+} complexes is shown in figure 9.

Pr^{3+} has been used to study the complexational characteristics of lasalocid by ^1H and ^{13}C NMR to show that it forms an equimolar complex (Chen and Springer 1978). Our circular dichroism (CD) results on the lanthanide complexes of lasalocid show a dependence on the size of the cation—a manifestation of the lanthanide contraction (Shastri and Easwaran 1985). Gd^{3+} and Mn^{2+} have also been shown to bind to lasalocid (Hanna *et al* 1983) by their effect on the ^{13}C NMR spin-lattice relaxation times. The binding sites have been shown to be determined by the cation charge and solvent polarity. We have also shown that valinomycin complexes with Mn^{2+} and forms both equimolar and ion-sandwich complexes by EPR spectroscopy (Sankaram and Easwaran 1982). The Mn^{2+} EPR spectral changes upon addition of valinomycin are shown in figure 10.

11. Conclusions

Paramagnetic probes *viz* covalently and non-covalently attached spin-labels, lanthanide ions etc are very useful probes of the structure and dynamics of membranes. Membrane fluidity, lipid motions, lipid bilayer phase transitions, membrane permeability and conformations of cation mediators can be studied in detail by the use of these probes in EPR and NMR spectroscopy. Further advances in the areas of



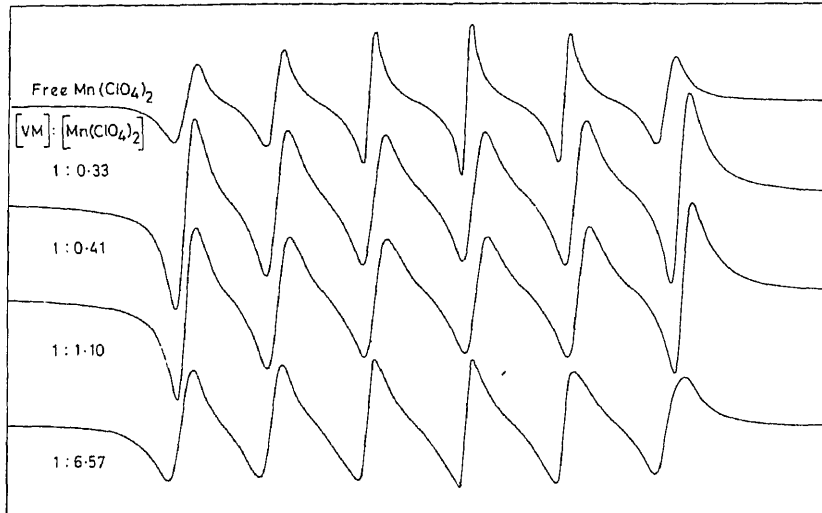


Figure 10. EPR spectra of Mn^{2+} upon addition of carrying amounts of valinomycin in acetonitrile at 25°C . $[\text{Mn}(\text{ClO}_4)_2] = 5 \text{ mM}$.

lipid-protein interactions and transmembrane cation transport are rapidly taking place.

Acknowledgements

We recall with gratitude the discussions we had with the late Prof. R. Srinivasan in some of our studies described in this review, especially the EPR studies on manganese complexes of valinomycin.

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Heisenberg spin exchange and chemical electron exchange in naphthalene negative ion—An electron spin-lattice relaxation study

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Abstract. Electron spin-lattice relaxation times (T_{1e}) as determined by saturation recovery technique and linewidths have been investigated as a function of the concentration of naphthalene anion and the unreduced naphthalene in dimethoxyethane from conditions of slow exchange to fast exchange. It was observed that Heisenberg spin exchange was more effective in determining T_{1e} and linewidth than chemical exchange at comparable concentrations. Contrary to earlier findings, T_{1e} was found to depend on the radical concentration even at the fast exchange regime.

Keywords. Electron spin-lattice relaxation; ESR; chemical exchange; Heisenberg exchange; aromatic anions; naphthalene negative ion; saturation recovery technique.

1. Introduction

During our current systematic study of the electron spin lattice relaxation times (T_{1e}) of aromatic negative ions by the saturation recovery technique, we have made some interesting observations on the dependence of T_{1e} on the concentration of the radical anions. It has been recognised for several years that intermolecular electron spin exchange reactions between radicals (Heisenberg exchange) and electron exchange between the radical and their diamagnetic precursors (chemical exchange) are relaxation mechanisms and contribute to ESR linewidths and T_{1e} 's (Anderson 1954; Ward and Weissman 1957; Piette and Anderson 1959; McConnell 1958; Swift and Connick 1962; O'Reilly and Poole 1963; Sohma 1962; Freed 1967). The rate of chemical exchange between naphthalene anion and neutral naphthalene has been determined as early as 1957 by a study of the dependence of ESR linewidth on the concentration of the neutral species (Ward and Weissman 1957). Similar studies on sulphur radical have been reported (Gardner and Fraenkel 1956). However, the effect of such chemical and Heisenberg exchange on T_{1e} has been poorly understood.

In our laboratory it has been demonstrated that T_{1e} of semiquinone, as measured by saturation recovery technique, are independent of the free radical concentration in alcoholic solvents but strongly dependent on the radical concentration in aprotic solvents such as acetonitrile and tetrahydrofuran (Rengan *et al* 1974a, b). This observation was presumed to indicate the presence of a solvent cage around the free radical due to hydrogen bonding in alcohols leading to decreased probability of encounter between free radicals; at similar concentrations of free radicals, the rate of intermolecular encounters is normal when the solvent cage is absent in the aprotic solvents. Cheng and Weissman (1976) have measured T_{1e} 's in solutions of potassium tetracyanoethylene containing neutral tetracyanoethylene (TCNE) by progressive

saturation technique. These studies paralleled those of Eastman *et al* (1969) wherein the stress was on the study of Heisenberg spin exchange between TCNE^- radicals, rather than chemical exchange. Percival and Hyde (1976) have attributed the concentration dependence of T_{1e} of nitroxides to electron-electron dipolar coupling modulated by translational diffusion. They conclude that Heisenberg spin exchange, which makes an important contribution to the linewidth, is a pseudo-secular process and thus does not affect T_{1e} . Owing to the paucity of data on longitudinal relaxation times, T_{1e} , our understanding of the effect of Heisenberg and chemical exchanges on T_{1e} is rather poor. The conclusions reached with T_{1e} determined by progressive saturation technique, are circumspect since the quantity measured experimentally by the CW technique is T_{1e}^{eff} , which includes contributions from various pseudo-secular processes (Percival and Hyde 1976). In the pulsed saturation recovery method, which is being practised by only a few groups (Rengan *et al* 1974; Percival and Hyde 1976; Fessenden *et al* 1981), T_{1e} is measured directly.

The effect of Heisenberg and chemical exchange is manifested most dramatically in the linewidths of ESR spectra. In the slow exchange regime, both of the exchanges broaden first the individual hyperfine lines. With the increase of exchange rates, all the hyperfine lines merge to a single broad line. With further increase of exchange rate, the broad line starts narrowing and at extremely high rate, a single exchange narrowed Lorentzian line results. Freed and coworkers (Eastman *et al* 1969) have shown experimentally and theoretically that in the slow exchange regime T_{1e}^{eff} of TCNE^- decreases with increase in concentration of the radical. Cheng and Weissman (1976) conclude that in the case of slow exchange between $\text{K}^+ \text{TCNE}^-$ and TCNE , T_{1e}^{eff} decreases with increase of TCNE concentration and that in the fast exchange regime $1/T_2$ is proportional to the reciprocal of the concentration of TCNE while T_{1e} is independent of the same. The physical explanation of T_{1e} 's being independent of concentration in the fast exchange limit in both Heisenberg and chemical exchanges, is that all the hyperfine lines saturate equally because of rapid exchange of spins among themselves and the measured T_{1e} should thus be the intrinsic spin lattice relaxation. However, a careful analysis of these data (Cheng and Weissman 1976) shows some interesting discrepancies. Although they predict, from steady state solution of Bloch equations in the presence of chemical exchange, that T_{1e}^{eff} should first decrease with the increase of concentration of the diamagnetic molecule in the slow exchange regime and then revert to the intrinsic T_{1e} at the fast exchange regime and become independent of the concentration of the diamagnetic molecule, and conclude the same from their experimental findings, they have not reported any data indicating this inversion behaviour. Moreover, their results in the slow exchange regime show that in the limiting case where the concentration of TCNE goes to zero, the T_{1e} is approximately $3.3 \mu\text{sec}$. This value may be taken to be the intrinsic spin lattice relaxation time at -9.2°C . On the other hand, they publish T_{1e} 's at the fast exchange regime at different temperatures from which one finds that T_{1e} increases with the increase of temperature; and since according to this T_{1e} is $1.76 \mu\text{sec}$ at 30.0°C , it will certainly not be $3.3 \mu\text{sec}$ at -9.2°C .

The instrument used for the saturation recovery studies (Das *et al* 1985) was a home-built spectrometer similar to the one described by Fessenden *et al* (1981). The observed power and the pump power level could be independently controlled. The separation of the free induction decay signal and the saturation recovery signal from the observed M_y component of the magnetisation has been achieved by performing two sets of experiments with the phase of the pump power being changed by π radian between the two sets as has been suggested by Percival and Hyde (1975).

2.2 CW ESR spectrometer

For linewidth and intensity measurements of the ESR spectra, we used a modified Varian V4500 100 kHz field modulated x-band spectrometer (Khakhar *et al* 1966).

2.3 Chemicals

Commercial naphthalene was used after vacuum sublimation. The solvent dimethoxyethane (DME) from Aldrich Chemical Co., Inc., was distilled from sodium and dehydrated by lithium aluminium hydride. It was then vacuum-distilled into a vessel containing a sodium mirror and anthracene. Deep green colour of anthracene dianion showed that the solvent was free from oxygen or any other paramagnetic impurity.

2.4 Sample preparation

The negative ion radical of naphthalene was prepared by the alkali metal reduction process. To make the dilution of the solution so prepared easier by vacuum distillation, we have found it convenient to use a modified form of sample tube as shown in figure 1. The tube and the vessel at F were calibrated and could hold about 5 ml of liquid. The vessel E is a large bulb of 10 ml capacity. D is a small bulb attached to a narrow tube where a small piece of sodium was kept. The whole apparatus was then connected to a vacuum line through the standard joint A, keeping the vessel F in liquid nitrogen, which contained a known amount of naphthalene. After evacuating to about 10^{-3} torr, the sodium in D was gently evaporated and allowed to form a mirror just below the constriction B. The side arm was then disconnected from the main tube by sealing it at the constriction C. Some amount of DME was then brought to the vessel F by keeping it in liquid nitrogen and distilling under vacuum from a DME storage vessel already connected to the vacuum line. The amount of solvent transferred could be estimated from the graduation on this arm. The solvent was then degassed 3 times by 'freeze, pump and thaw' technique and eventually disconnected from the vacuum line by sealing it at the constriction B. Reaction took place when the dissolved naphthalene was brought in contact with the sodium mirror. It was left overnight in that position for the reaction to reach equilibrium. The advantage of the large vessel may now become apparent. If we want to dilute the sample by a factor of 2, say, we transfer about half the bulk solution to this vessel and keep F in liquid nitrogen. Only the solvent will then distill from E to F. The large volume of E will prevent the radical from going accidentally to the other side, even if the solution 'bumps' while distilling. The diluted solution in F may be made homogeneous by shaking and the resulting solution may be

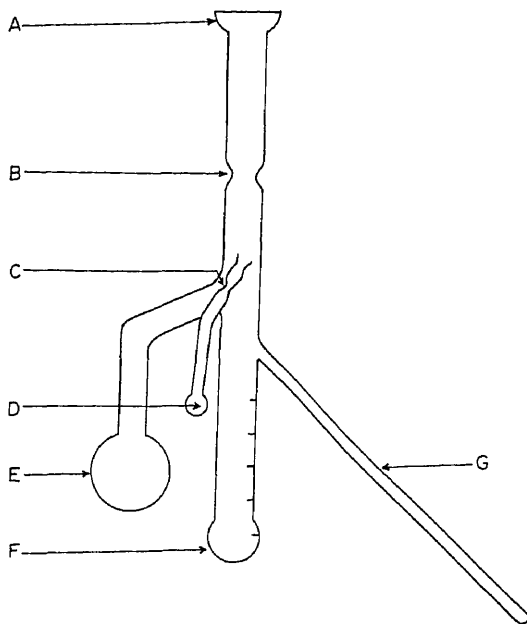


Figure 1. ESR sample tube: A—Standard joint; B, C—constrictions for sealing; D, E, F—storage bulbs; G—4 mm O.D. narrow tube for ESR measurement.

taken to the narrow tube G for ESR measurements. On the other hand, if we want to increase the concentration, we keep the vessel E in liquid nitrogen, so that only the solvent distils from F to E, and thus increases the concentration of the solution in F. The important point to be noted here is that, by this process we change the concentration of the radical as well as the neutral molecule maintaining their ratio constant.

Concentration of the naphthalene radical was estimated by comparing its signal intensity with that of a standard 1.1 mM 4-hydroxy-2,2,6,6-tetra-methyl-piperidinoxy (TANOL) free radical recorded under similar conditions of the CW spectrometer. The formula used was (Poole 1967)

$$\frac{N^A}{N^B} = \frac{D^A}{D^B} \{ (\Delta H_{pp}^A)^2 (Y_m^A / H_{mod}^A) \} / \{ (\Delta H_{pp}^B)^2 (Y_m^B / H_{mod}^B) \}.$$

where N^i is the number of spins of the i th species whose degeneracy is D^i , first derivative peak-to-peak width ΔH_{pp}^i , peak-to-peak height Y_m^i for the field modulation amplitude H_{mod}^i . We determined the (Y_m^i / H_{mod}^i) factor by recording the first derivative spectra for different modulation amplitude. Lorentzian line shape was assumed for the TANOL and the naphthalene spectra that we have studied in the exchange narrowed region.

3. Results and discussion

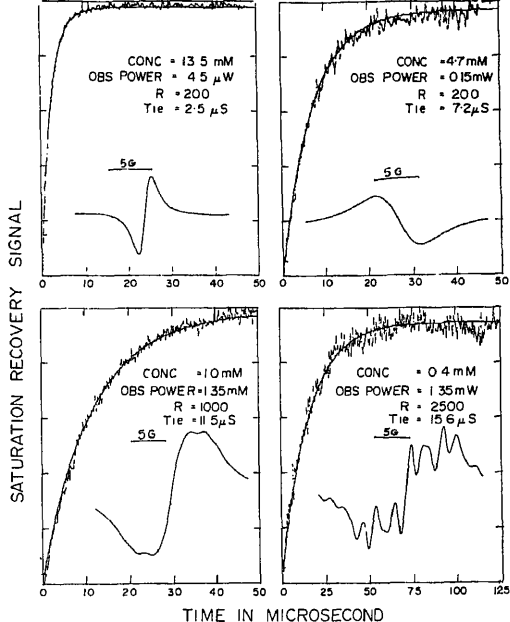


Figure 2. Saturation recovery curves for Na^+ naphthalene $^-$ in DME solution at 23°C for different dilutions. In each of them, the CW spectra are also depicted to indicate the change in line shapes with dilution. The noisy trace is the average signal of R experiments, while the smooth curves superimposed on them are fits to a single exponential with characteristic T_{1e} 's.

The different curves in figure 2 correspond to concentrations of the free radical varying from about 13 mM to 0.5 mM. It is observed that in all the cases the saturation recovery is exponential. Since the observed T_{1e} usually depends upon the level of microwave power used to observe the recovery from saturation it is customary to measure T_{1e} as a function of the observing microwave power and estimate the true T_{1e} from the limiting value at zero observing power, from a $1/T_1$ vs (observe power) $^{1/2}$ plot (Atkins *et al* 1973). However it was observed that T_{1e} was constant within error limit between 2.0 mW to 20 μW of observing power for all the samples studied here. T_{1e} estimated in this manner was accurate to better than 10%. It may be noticed (figure 2) that the exponential nature of the recovery was followed from the slow exchange, where hyperfine structure was observed, to the fast exchange regime, where the hyperfine structure had been completely washed out resulting in a single narrow line.

Several samples with different initial concentration of naphthalene were investigated to determine the effect of Heisenberg exchange and the chemical exchange. The samples were diluted as described earlier keeping the ratio of $[\text{C}_{10}\text{H}_8^-]$ to $[\text{C}_{10}\text{H}_8]$ constant. In figure 3 the derivative peak-to-peak linewidths, ΔH_{pp} 's are plotted as a function of the naphthalene radical concentration for different samples with different amounts of unreacted naphthalene. It is indeed surprising that all the points fell on the same straight line, irrespective of the unreacted naphthalene concentration. All the points followed equation of the type

$$\Delta H = \Delta H_0 + \frac{A}{C} \quad (1)$$

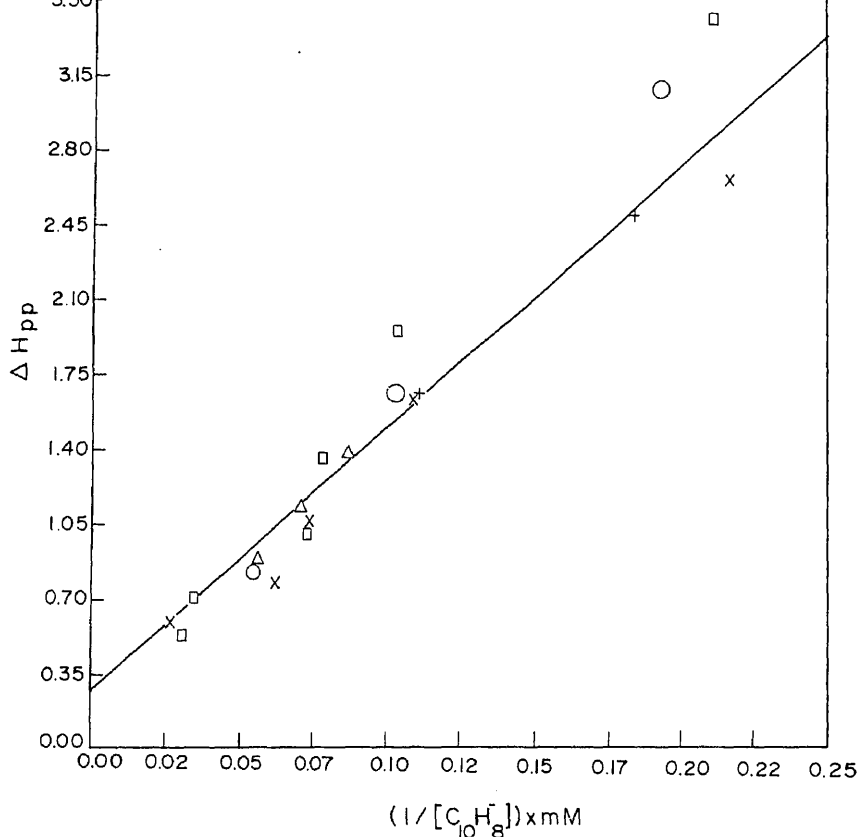


Figure 3. Plot of exchange narrowed peak-to-peak first derivative linewidths of Na^+ Naphthalene $^-$ at 23°C as a function of reciprocal of the radical concentration for different samples differing in $[\text{C}_{10}\text{H}_8^-]$ to $[\text{C}_{10}\text{H}_8]$ in the equilibrium reaction mixture (see figure 4 for these concentrations). The ΔH_{pp} 's were measured in units of ΔH_{pp} of TANOL.

for the fast exchange regime (Molin *et al* 1980, p. 119). We had expected to find different curves for different initial concentration of naphthalene. However, it is to be noted that narrowing due to chemical exchange for this system is seen only at concentrations of naphthalene close to 100 mM (Ward and Weissman 1957). Apparently the narrowing observed in our case may be due to fast Heisenberg exchange which was manifested even at millimolar concentrations of the radical $\text{C}_{10}\text{H}_8^-$.

Dependence of T_{1e} on $[\text{C}_{10}\text{H}_8^-]$ is shown in figure 4. It appeared to follow an equation of the type

$$\frac{1}{T_{1e}} = \frac{1}{T_{1e}^0} + K_e C, \quad (2)$$

where $1/T_{1e}^0$ is the intrinsic spin lattice relaxation time, K_e the exchange rate constant and C the concentration of the radical. This equation is true only in the case of *slow* exchange of Heisenberg type (Molin *et al* 1980b, p. 521 eq 2, 104). This figure shows that

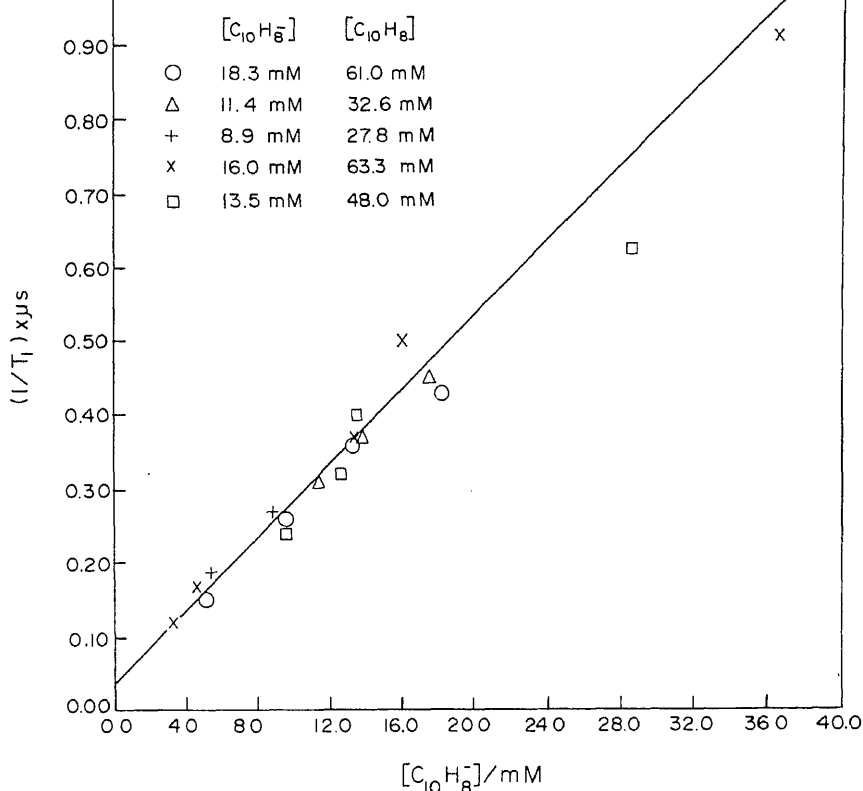


Figure 4. Dependence of $1/T_{1e}$ on $[C_{10}H_8^-]$ for different samples whose compositions of the equilibrium reaction mixtures are given at the top left corner.

the relaxation time T_{1e} was influenced mainly by the radical concentration and not by its diamagnetic precursor. It is further surprising that while earlier theory expects T_{1e} to be independent of the radical concentration in the fast exchange regime, we found T_{1e} to be dependent on it.

To further illustrate that the radical concentration $[C_{10}H_8^-]$ plays the dominant role in determining linewidth by Heisenberg exchange, we have measured the concentration and ESR linewidth as a function of time while allowing the naphthalene to react with the sodium mirror in the sample tube. Periodically the solution was removed from contact with the sodium mirror and measurement made (figure 5). We observed the narrowing of linewidth as the concentration of $C_{10}H_8^-$ increased with time. It should be emphasised that we always observed an unresolved broad line even at low radical concentration indicating that chemical exchange between $C_{10}H_8^-$ and $C_{10}H_8$ was present. It is, however, clear from this observation (figure 5) that Heisenberg exchange manifested itself at much lower radical concentration as compared to the concentrations required for effective chemical exchange.

In order to get a well-resolved spectrum, both $[C_{10}H_8^-]$ and $[C_{10}H_8]$ have to be low. In order to achieve this, the reaction mixture which had reached equilibrium after some

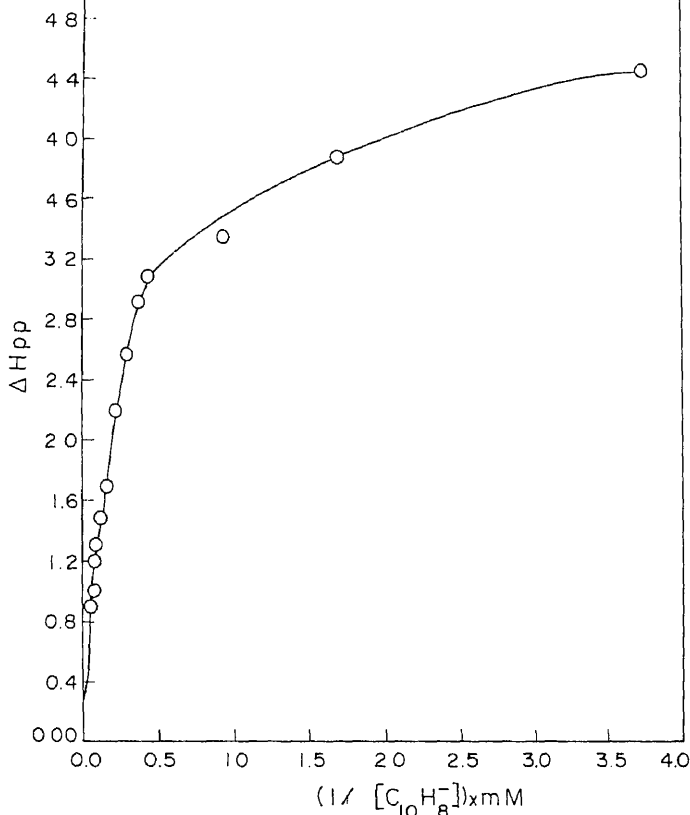


Figure 5. Dependence of peak-to-peak first derivative linewidth ΔH_{pp} as a function of naphthalene radical concentration during the progress of the reaction of naphthalene with sodium mirror. ΔH_{pp} 's were measured in units of ΔH_{pp} of TANOL.

time, had to be diluted adequately as described earlier thereby reducing both the concentrations. In such very dilute solutions, we were able to observe even the ^{23}Na hyperfine splittings in DME as solvent (figure 6) contrary to the finding of Atherton and Weissman (1961).

Mere applicability of equation (1) is not by itself an evidence of narrowing of lines brought about by bimolecular collision of particles causing exchanges of electron spins. For very concentrated solutions, exchange narrowing of ESR lines may occur as a result of the same mechanism as in the solid state where collisions of particles do not take place. It has been shown to be the case both by theory (Kivelson 1960) and by experiment (Molin *et al* 1980, p. 119) on aqueous solution of $\text{Cu}(\text{NH}_3)_5^{2+}$. This is termed as the static spin exchange for which the coefficient A in equation (1) does not depend upon temperature or viscosity of the solution. Thus in order to ascertain that our experiments were showing the exchange narrowing brought about by dynamic bimolecular collision, we proceeded as follows:

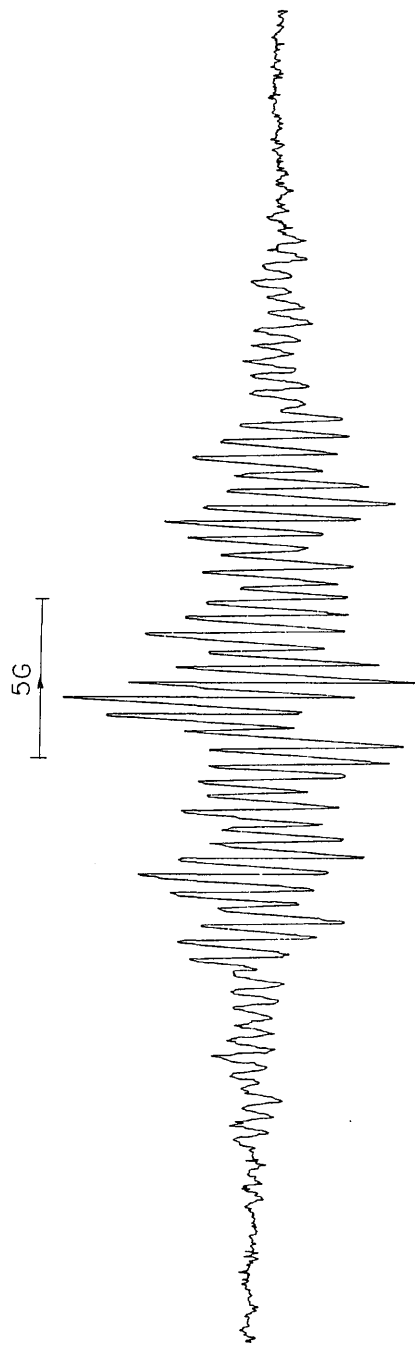


Figure 6. CW ESR spectrum of $\text{Na}^+ \text{C}_{10}\text{H}_8^-$ in DME at 23°C showing the hyperfine splittings of ^{23}Na .

The complete form of (1) for bimolecular collision is (Molin *et al* 1980, p. 117)

$$\Delta H = \Delta H_0 + 3.39 \times 10^6 \times g \sum_i I_i (I_i + 1) (\Delta H_{hf}^i)^2 / K_e C. \quad (3)$$

When g is the g -value of the radical with concentration C , ΔH_{hf}^i is the hyperfine coupling constant of the i th nucleus with nuclear spin I_i , K_e is the exchange rate constant. Keeping in mind that the rate constant follows the usual Arrhenius equation

$$K_e = a_0 \exp(-\Delta E/RT),$$

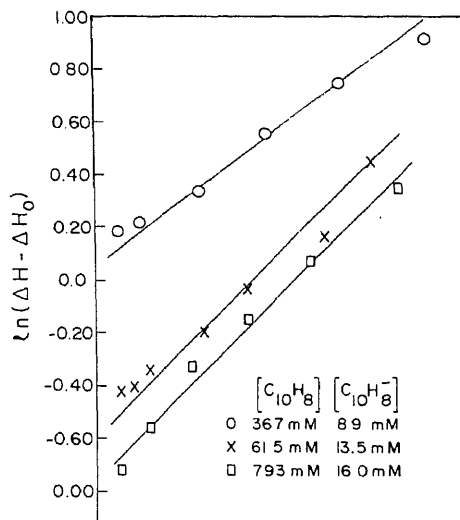
where a_0 is the pre-exponential factor, ΔE the activation energy, the other terms having the usual meaning, we may approximately write the temperature dependence of ΔH as

$$\Delta H = \Delta H_0 + \frac{A}{Ca_0} \exp(\Delta E/RT),$$

or

$$\ln(\Delta H - \Delta H_0) = \ln A - \ln a_0 - \ln C + \frac{\Delta E}{RT}. \quad (4)$$

Thus a plot of $\ln(\Delta H - \Delta H_0)$ should be linear in $1/T$ with a positive slope. Figure 7 shows such plots for three different samples. ΔH_0 for these plots was taken from the intercept of figure 3. The three plots are indeed linear and parallel to each other within experimental error. It may also be noted that the intercept follows the $-\ln C$ term of (4). This observation coupled with the one shown in figure 3, confirmed that we were



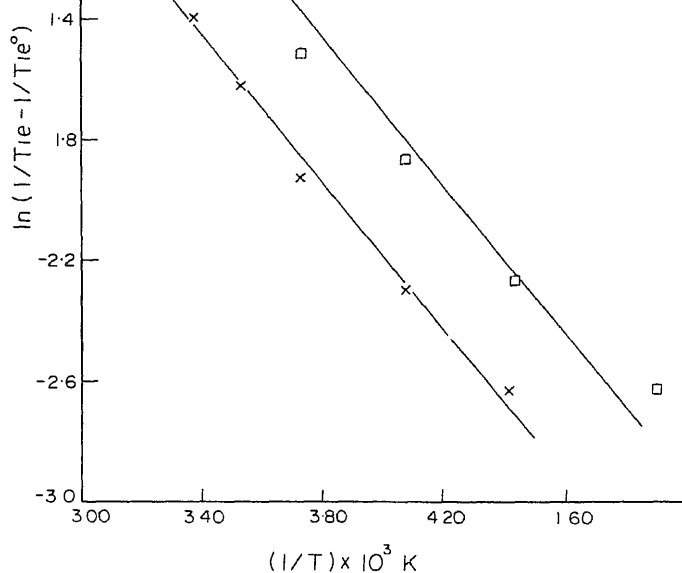


Figure 8. Plot of $\ln(1/T_{1e} - 1/T_{1e}^0)$ as a function of reciprocal of absolute temperature for two different samples with different ratios of $[C_{10}H_8^-]$ to $[C_{10}H_8]$.

serving phenomena brought about by binary collision of radicals in the fast exchange time.

Applying the same arguments as above on (2) we could derive an approximate temperature dependence of T_{1e} . Applying the Arrhenius equation to the rate constant, we may write

$$\ln(1/T_{1e} - 1/T_{1e}^0) = \ln a_0 + \ln C - \frac{\Delta E}{RT}. \quad (5)$$

Figure 8 shows such plots of two different samples where T_{1e}^0 was taken from the intercept of figure 4. They are again parallel and the slope (1.2×10^3) has approximately the same magnitude as that obtained from figure 7 (0.9×10^3), but opposite in sign, implying an activation energy of 2.0 kcal/mol. Thus the mechanism responsible for broadening of linewidth was also responsible for the change in the spin lattice relaxation times.

Conclusions

We have established that the Heisenberg spin exchange is more effective than chemical exchange at comparable concentrations for naphthalene anion radical and neutral

naphthalene system. Within the range of concentrations, we always found T_{1e} to be dependent upon the radical concentration even though it was firmly established that fast exchange was present in these concentration ranges. Earlier theory and experiment predict that T_{1e} should be independent of radical concentration in the fast exchange regime. In our case, however, it is necessary to differentiate between dipolar effects on T_{1e} from exchange effects before any conclusion can be arrived at. The processes that contribute to T_{1e} and linewidths in the fast exchange limit are similar since they showed the same temperature dependence with identical activation energy. A better understanding would emerge only when systems with simpler ESR spectrum (like TCNE $^-$) are investigated by saturation recovery technique in the presence of chemical and/or Heisenberg exchange processes.

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On the indirect determination of ESR g -factors by NMR of paramagnetic crystals

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Abstract. Single crystal proton broadline NMR of the Tutton salt $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is reported. From the analysis of the water proton dipolar tensor proton positions have been located, based on hydrogen bonding schemes. Besides, from an analysis of the paramagnetic proton shift tensors the g -tensor of the $[\text{Co}(\text{H}_2\text{O})_6]$ chromophore has been evaluated. Comparison with directly measured g -tensor at 4.2 K is found to be good.

Keywords. Broadline NMR; paramagnetic shift tensor; g -tensor; paramagnetic resonance.

1. Introduction

The line shape and width of nuclear magnetic resonance absorption in solids depend on the magnetic field inhomogeneity and dipolar interaction of the surrounding magnetic nuclei with the resonant nuclei. The second moment analysis in solids will give information about the dipole-dipole interaction (Van Vleck 1948). If the dipole-dipole interaction is larger than the linewidth one can observe dipole split line and this was observed first in proton magnetic resonance study of hydrated gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystal by Pake (1948). Later many authors (Pedersen and Holcomb 1963; Padmanabhan *et al* 1974) extended this technique to hydrated salt crystals to determine directions of the water protons and their positions.

In most of the hydrated salt crystals, the water molecules at ambient temperatures undergo a flipping motion about the bisector of the HOH angle (Ketudat *et al* 1956), resulting in two dipolar split lines for each water molecule as a result of magnetic equivalence of the two protons in diamagnetic systems. This motion can be arrested by cooling the system down to low temperatures. Bloembergen (1950) observed ten unresolved component lines in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 4.2 K due to the non-equivalence of the water protons in this paramagnetic host. In diamagnetic lattices, however, these dipolar split lines will occur symmetrically about the free proton resonance. This interaction, being purely dipolar, follows a $(1-3 \cos^2 \theta)/r^3$ dependence. With the chemical intuition about hydrogen bonding schemes and by following the dipolar splitting of the proton resonance lines in hydrated salts as a function of crystal orientation one can easily map out the proton positions which are otherwise very difficult to accurately determine by x-ray diffraction. Only neutron diffraction can give precise positions of the protons. In cases where neutron diffraction data is not available, broad line NMR is a tool to elucidate proton positions accurately in hydrated crystals.

Although diamagnetic salt hydrates have been subjected to broad line measurements, very little work has been done in paramagnetic salt hydrates where the centre of gravity

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paramagnetic metal ion. This shift is anisotropic in nature. In many high spin non S-state ions due to fast spin lattice relaxation ESR measurements have to be carried out at ultra-low temperatures. However, proton NMR can be done at room temperature and the very process which makes EPR spectra unobservable at room temperature makes NMR of lattice protons observable. So in paramagnetic salt hydrates apart from locating precisely the proton positions one can get the shift tensor (Padmanabhan *et al* 1974; Sato *et al* 1980; Raj *et al* 1982) and hence indirectly the g -tensor of the paramagnetic moiety.

In this paper we estimate g -tensor in $K_2Co(SO_4)_2 \cdot 6H_2O$ by analysing the paramagnetic shift tensor and proton positions. The present system, however, contains twelve water molecules per unit cell, of which six are magnetically distinct in general orientations except for b -axis rotation. Accurate analysis of the dipolar anisotropy and shift tensor is difficult due to many overlapping features. However, it is shown that fairly reliable g -values can be extracted from measurements of paramagnetic hydrated salts. Chidambaram and Raghavarao (1963) reported the direction cosines of the p - p -vectors in the isomorphous diamagnetic zinc and magnesium tutton salts.

2. Theory

The dipolar splitting between the two proton lines in a water molecule can be given by

$$\Delta B = 2\alpha[3 \cos^2 \theta_{12} - 1], \quad (1)$$

where $\alpha = 3/2 \mu r_{12}^{-3}$ in which μ is the proton magnetic moment, r_{12} is the distance between two protons and θ_{12} is the angle between the applied magnetic field B_0 and proton-proton (PP) vector. By transforming into laboratory coordinate system XYZ

$$\Delta B = 2\alpha[3 \cos^2(\phi - \phi_0) \cos^2 \delta - 1], \quad (2)$$

where δ is the angle between the PP vector and the plane perpendicular to the rotation axis, ϕ is the angle between B_0 and reference axis attached to the crystal and lying in the plane perpendicular to rotation axis and ϕ_0 is the angle between projection of the PP vector onto the above plane and reference axis (see figure 1). δ and ϕ_0 can be measured by rotating the crystal about a known crystallographic axis.

In the case of paramagnetic crystals the centre of gravity of the two lines from a particular water molecule will be shifted due to the dipolar field arising from the magnetic susceptibility of the metal ion as well as any transferred spin density onto the protons *via* the chemical bonds, though transferred spin density interaction is usually small and is a measure of contact hyperfine interaction at the site of proton. The susceptibility interaction is anisotropic in nature and the total shift B_s can be given as

$$B_s = a I \cdot S + \frac{\chi \cdot B_0}{R_{M-H}^3} (1 - 3 \cos^2 \omega), \quad (3)$$

where a is isotropic hyperfine coupling constant, χ is the susceptibility tensor and R_{M-H}^3 is the distance between metal ion and proton, ω being the angle between M-H direction and applied magnetic field. Expressing in terms of g -tensor, the anisotropic contribution can be written as

$$B_{s,c} \text{ (in gauss)} = \frac{g^2(\phi) \beta^2 \hat{S}(\hat{S} + 1) (1 - 3 \cos^2 \omega)}{R_{M-H}^3} B_0. \quad (4)$$

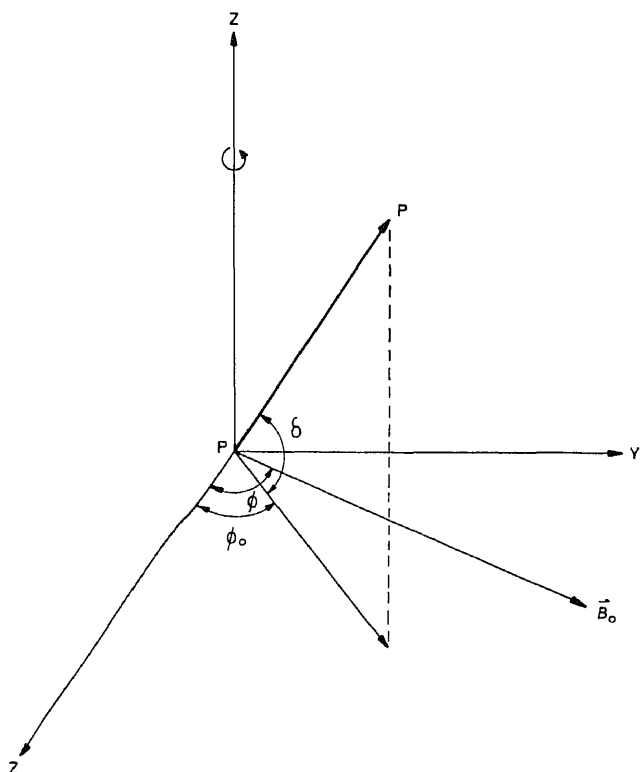


Figure 1. Representation of P-P vector in the laboratory coordinate system.

where $g(\phi)$ is the g -effective at a particular orientation of B_0 , β is the Böhr magneton, k is Boltzman constant, T is the temperature and $\hat{S}$ is the fictitious spin angular momentum of the electron. In the case of paramagnetic ions with $S > \frac{1}{2}$ one has to use fictitious spin e.g. for Co^{2+} high spin $\hat{S} = \frac{1}{2} \cdot g^2(\phi)$ can be expressed as

$$g^2(\phi) = g_{11}^2 \cos^2 \phi_1 + g_{22}^2 \cos^2 \phi_2 + g_{33}^2 \cos^2 \phi_3. \quad (5)$$

ϕ_1, ϕ_2, ϕ_3 are the angles between B_0 and g_{11}, g_{22}, g_{33} , directions. The anisotropic susceptibility shift tensor will be traceless only when g -tensor is isotropic. The trace of χ is due to the isotropic shift contribution from g -anisotropy. Since trace need not be zero as in most cases, it is difficult to exactly estimate isotropic transferred spin density contribution from the total centre of gravity shift (i.e. the experimental shift tensor).

Experimental

Large single crystals of $\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ of $10 \times 8 \times 8$ mm size were grown from aqueous solution containing stoichiometric quantities of K_2SO_4 and $(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$. The morphology of representative small crystals was determined using Enraf Nonius CAD-4 x-ray diffractometer. The morphological characteristics are

$\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Kannan and Viswanatha 1965). Experiments were carried out on WL-210 wideline accessory of the Varian E-112 spectrometer. Measurements were done at 30 MHz. The crystal was fixed to the goniometer by means of quickfix and the quickfix proton signal was considered as the reference zero. Spectra were recorded for every 10° interval (for every 5° in some orientations) in three mutually perpendicular a , b , c^* ($=a \times b$) planes at room temperature. In b axis rotation, only three pairs of lines were observed implying that only three PP vectors out of twelve per unit cell are magnetically distinct. But in a and c^* rotations at arbitrary crystal orientations six pairs of lines were observed. Out of six pairs, two pairs most of the time get overlapped with other pairs.

The angular variation of proton peak positions in a and c^* axes rotations is shown in figures 2 and 3 respectively. Only 5 pairs for a axis and 4 pairs for c^* and all the 3 pairs for b axis rotation are followed. These experimental points are least square-fitted to following equation.

$$H = A\cos^2\psi + B\sin 2\psi + C, \quad (6)$$

where ψ is the laboratory rotation angle. These lines are asymmetrically shifted around free proton line due to paramagnetic shifts. But pair separation is not affected to first order by these shifts. Typical angular variation plots of pair separations for a and c^* rotations are shown in figures 4 and 5 respectively. The centre of gravity shifts for these

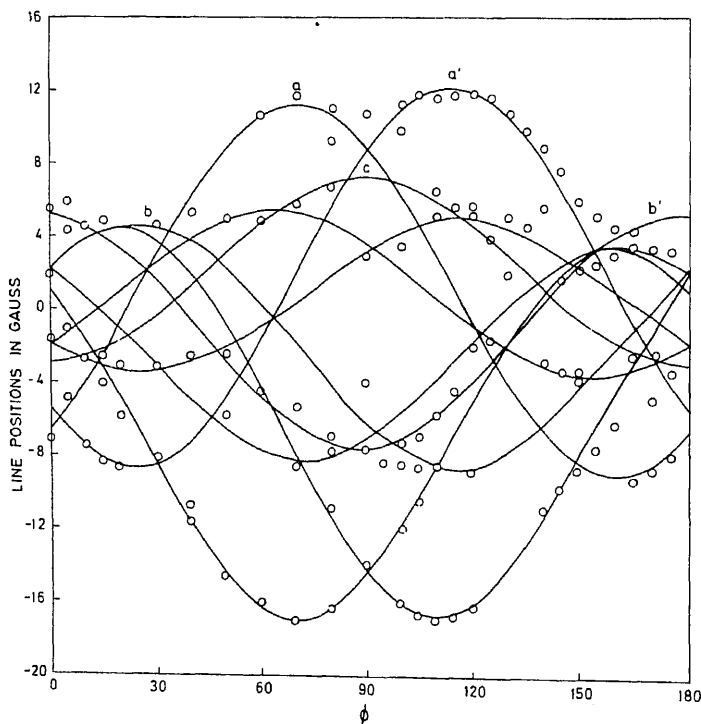


Figure 2. Angular variation of proton lines for a -axis rotation. Five pairs of resonances out of six expected could be followed in this rotation.

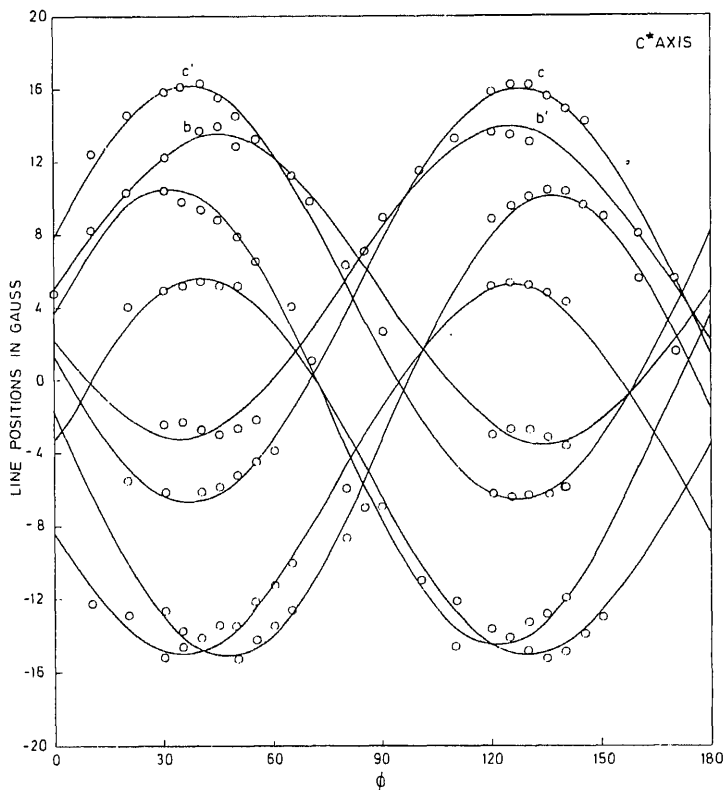


Figure 3. Same as in figure 2, but for c^* axis rotation. Only four pairs could be unambiguously identified.

rotations are shown in figures 6 and 7 respectively. Solid curves represent the theoretical and points the experimental values.

Discussion

3.1 Proton-proton vectors

When the pair separation was maximum, an exaggerated splitting was observed. This shift could be explained as due to the contribution from nonsecular terms which will shift both lines for a particular pair to the same distance in the opposite sign. This shift will be of the order of linewidth and this is also an angle and temperature-dependent factor. Considering a linewidth of 2 gauss, totally 4 gauss was subtracted from the maximum line separation and was used for calculating direction cosines of PP vector. The direction cosines of magnetically distinct PP vectors are listed in table 1. Other vectors can be generated using space group symmetry. Using the hydrogen bonding scheme introduced by El Saffar (1966) proton positions were calculated and these in fractional coordinates are listed in table 2. Hydrogen atoms H(1) and H(2) belong to

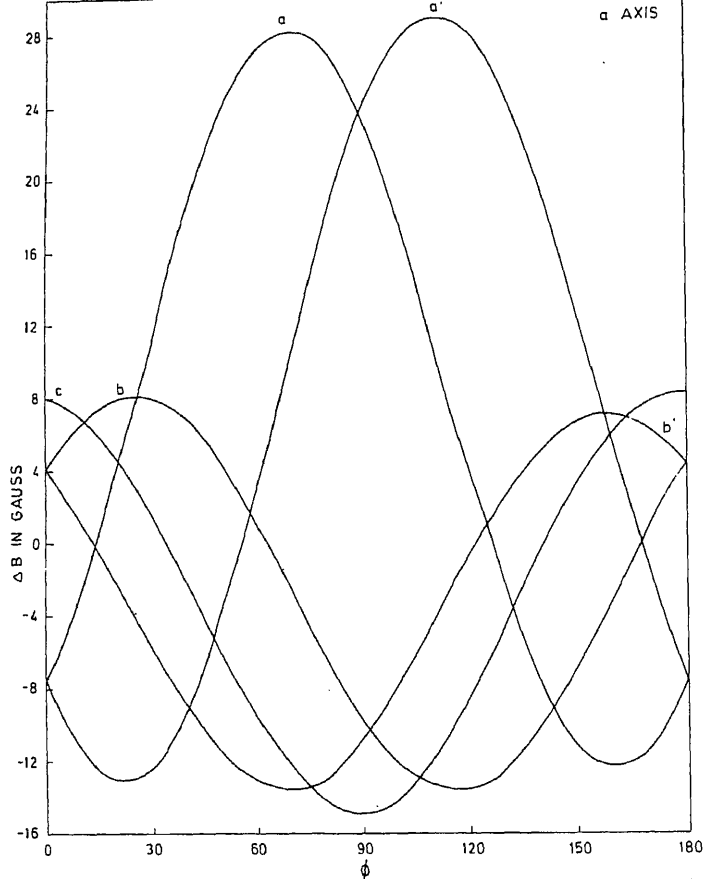


Figure 4. Angular variation of dipolar splitting for *a*-axis rotation for the five distinct P-P vectors.

4.2 *g*-tensor of the Co(II) moiety

Paramagnetic shifts also like any diadic symmetric tensor can be least square-fitted to equation (6). The coefficients *A*, *B* and *C* in each plane will give three of the shift tensor parameters. In case of *a* axis rotation

$$A = S_{aa},$$

$$B = S_{cc} - S_{bb},$$

$$C = S_{bc} - \frac{1}{2}S_{aa},$$

and by cyclic permutation in the other axis we can extract the elements of the shift tensor in laboratory frame. This is then diagonalised to get the principal values and the direction cosines of the so-called shift tensor. Because of the overlapping of lines we were not able to follow all pairs in three rotations. The principal values of paramagnetic shift tensor and its direction cosines for one such pair *c* are given in tables 3 and 4

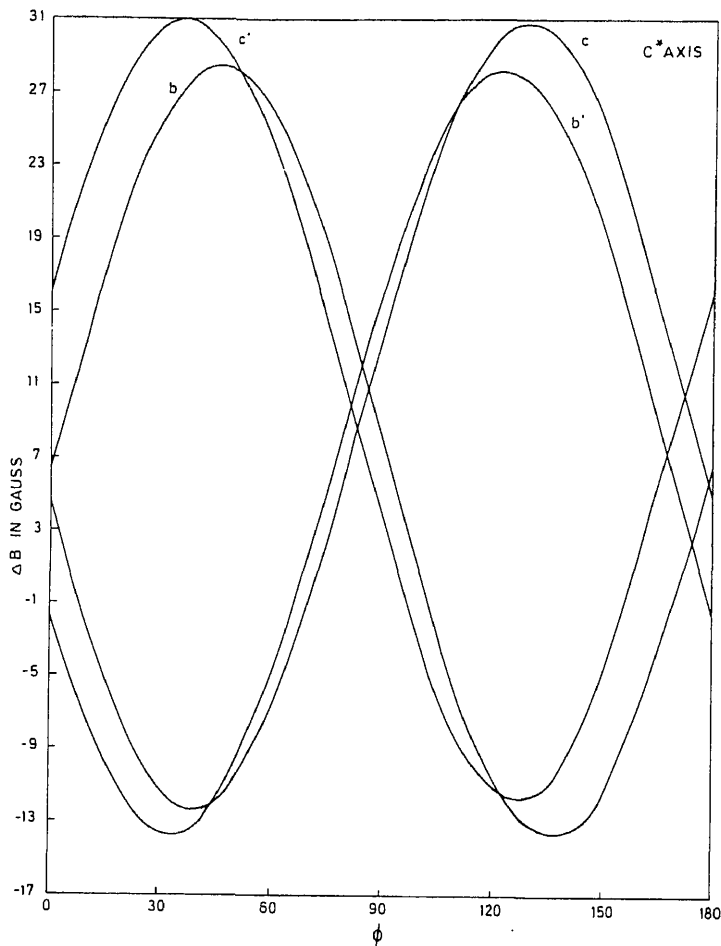


Figure 5. Same as in figure 4, but for c^* axis rotation for the four distinct P-P vectors.

These values are comprised of anisotropic susceptibility shifts and a pseudocontact shift and contact shift at the site of protons. The second term is very difficult to calculate from the principal values because the susceptibility tensor itself is non-traceless due to anisotropic g -value of cobalt. But ^{19}F NMR experiments by Harakawa (1964) on directly bonded fluorine to $3d$ metal ions showed the transferred spin density of the order of 0.5% equivalent to 5 gauss. Since in hydrated crystals water protons are not directly attached to metal ions we assumed 0.08% spin density and extracted the dipolar shift tensor based on this. It may be added here that similar transferred hyperfine density in the range of 0.02 to 0.1% is observed by ENDOR studies on $[\text{La}(\text{C}_2\text{H}_5 \cdot \text{SO}_4)_3 \cdot 9\text{H}_2\text{O}]$ (De Beer *et al* 1976).

4.3 Comparison with reported g -values

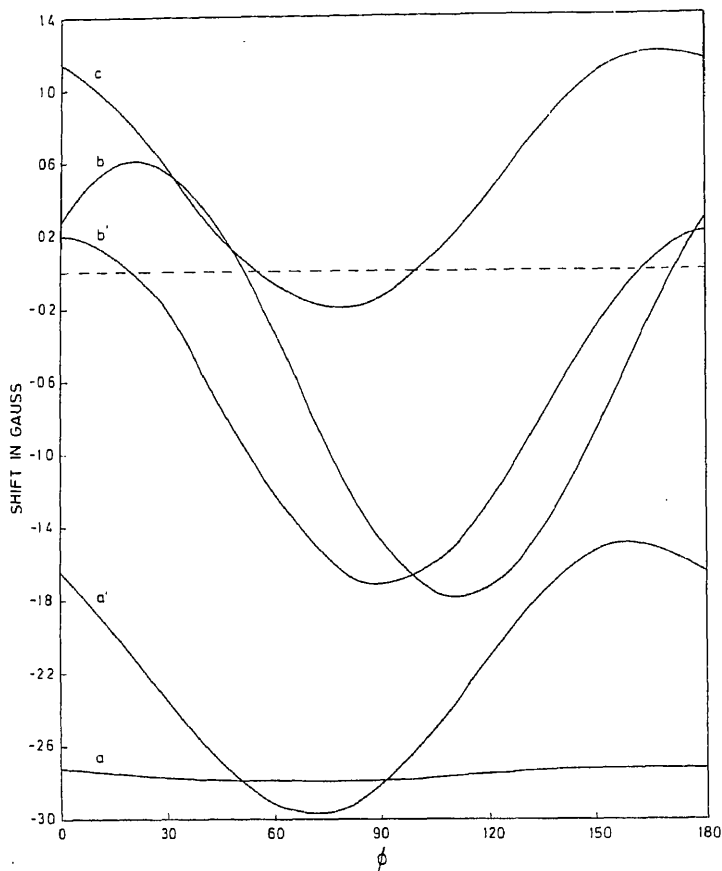


Figure 6. Angular variation of paramagnetic shift corresponding to the centre of gravity of the doublet dipolar lines for *a*-axis rotation.

and Pryce (1950). The reported values are

$$g_{xx} \geq 3.35; g_{yy} \leq 2.3 \text{ and } g_{zz} = 6.55.$$

Since the direction cosines of the cobalt(II) *g*-tensor are not reported, based on octahedral symmetry of the $[\text{CoO}_6]$ chromophore we have assumed different combinations of the *g*-tensor principal directions along Co-O₅, Co-O₆ and Co-O₇ directions and calculated the susceptibility shift tensor at both the protons of the water molecule. This was further averaged to consider the fast-flipping motion about C₂ of the water molecule. This shift tensor values for the combination which has g_{zz} along shortest Co-O direction was found to give shift tensor values in close agreement with the experimental values. The *g*-values were back-calculated from the experimental shifts and were close to that of EPR reported values at 4.2 K. The experimentally determined *g*-tensor principal values are

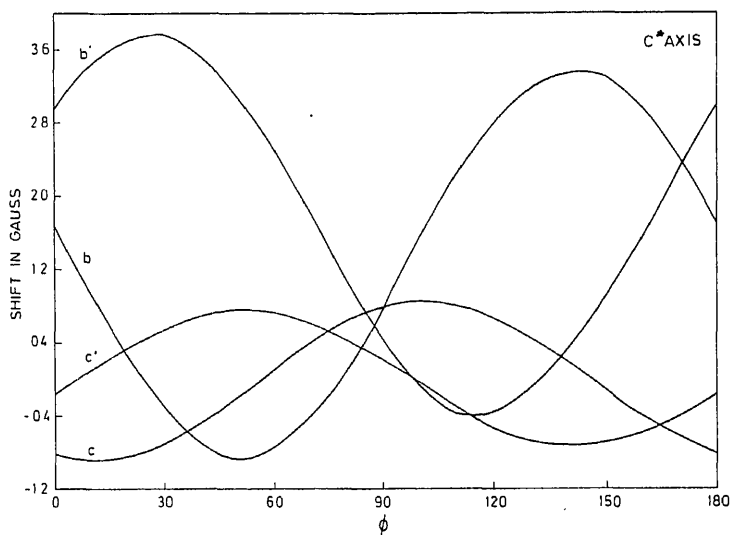


Figure 7. Same as in figure 6, but for c^* axis rotation.

Table 1. Magnitude and direction cosines of PP vectors.

PP Vector	PP distance			Direction cosines		
	A	ϕ_0	δ	a	b	c^*
a	1.43 ± 0.03	$70^\circ \pm 2^\circ$	$19^\circ \pm 2^\circ$	0.3256	0.3233	-0.8884
b	1.46 ± 0.03	$28^\circ \pm 2^\circ$	$43^\circ \pm 2^\circ$	0.6444	0.6837	0.3426
c	1.50 ± 0.03	$92^\circ \pm 2^\circ$	$40^\circ \pm 2^\circ$	-0.7656	0.6428	0.0267

Table 2. Proton positions in fractional coordinates derived from dipolar tensor.

Atom	x	y	z
H (1)	0.2567	0.1344	0.1040
H (2)	0.2417	0.0965	0.3187
H (3)	-0.1499	0.1914	0.0083
H (4)	-0.2701	0.1095	-0.0809
H (5)	-0.0992	-0.0655	0.3585
H (6)	0.0274	-0.1449	0.3517

5. Remarks and conclusions

Proton positions in paramagnetic hydrated crystals $K_2Co(SO_4)_2 \cdot 6H_2O$ were calcu-

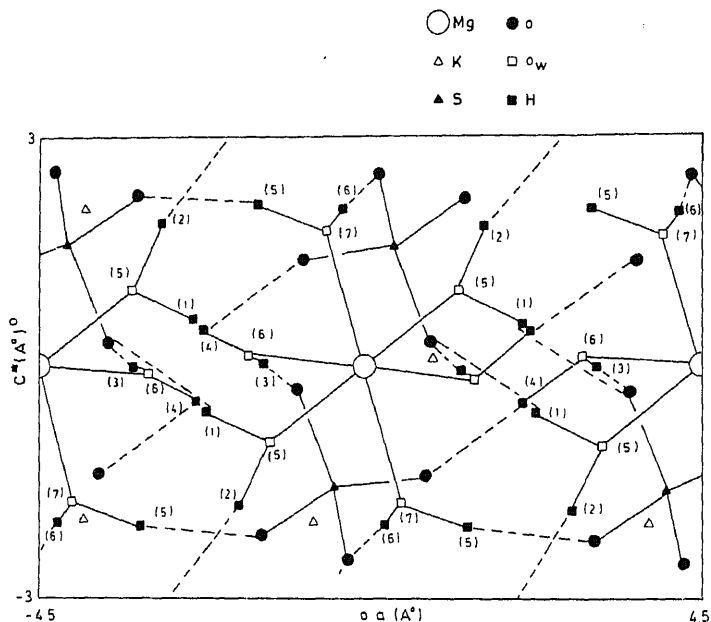


Figure 8. Projection of a unit cell of $K_2Co(SO_4)_2 \cdot 6H_2O$ lattice on to the ac^* -plane showing the derived proton positions and the hydrogen bonding schemes (dotted lines) derived from the NMR results. Filled circle represents oxygen atoms connected to sulphur while unfilled squares represent water oxygens.

Table 3. Shift parameters for PP vector c (all in gauss).

Principal values of shift tensor	B_s	B_{as}	B_{as} calc. using EPR parameters
S_{xx}	-1.3 ± 0.05	-2.1 ± 0.05	-2.2
S_{yy}	2.4 ± 0.05	1.6 ± 0.05	1.67
S_{zz}	0.823 ± 0.03	0.023 ± 0.03	0.025

Table 4. Direction cosines of shift tensor.

	a	b	c^*
S_{xx}	0.8745	-0.0621	-0.4811
S_{yy}	0.1401	0.9819	0.1278
S_{zz}	0.4644	-0.1792	0.8673

will be considered over-lapping of lines and the analysis will be difficult. In such cases experiments at high frequency and low temperatures like 77 K will give correct information, although the arresting of the water-flipping motion will lead to a doubling of the lines.

The interesting feature is that g -tensor is extracted for the pure system, while in EPR the presence of spin-spin interaction would entail diamagnetic dilution in an amorphous host lattice. And it is not always possible to retain the exact geometry of a dopant ion in a foreign lattice. An additional bonus comes by way of not requiring ultra-low temperature measurements. However, not all systems will be amenable since in some cases the spin lattice relaxation may not be ideal since further modulation *via* paramagnetic relaxation due to fluctuating dipolar interaction can give rise to considerable broadening, making accurate shift tensor measurements rather difficult. Nevertheless, it is pleasing to note that one could extract EPR parameters *via* NMR of a dipolar coupled neighbour.

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Abstract. The single crystal EPR results of $[\text{NiBr}_2(\text{diars})_2]\text{Br}$, a low spin Ni(III) complex, magnetically diluted in $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]\text{Br}$ show a very large bromine hyperfine coupling. The experimental g , ligand hyperfine splitting due to arsenic and bromine and spin densities are compared with other analogous diphos and diars complexes. The unpaired electron is essentially in the d_{z^2} orbital and there is extensive delocalization over all the ligand nuclei due to extended $4s$ and $4p$ radial wave functions. On the other hand the pure crystal of $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ shows single exchange averaged EPR line. Linewidth analysis using the existing theories of exchange gives values of roughly 800 G and 380 G for respectively isotropic and intersite exchange interactions in this system.

Keywords. Nickel diarsine complex; electron paramagnetic resonance; hyperfine splitting; exchange interactions; intersite exchange.

1. Introduction

Considerable single crystal EPR data on the six-coordinated low spin d^7 Ni(III) complexes of ligands *o*-phenylenebisdimethylphosphine(diphos) and *o*-phenylenebisdimethylarsine(diars) are available in literature (Kreisman *et al* 1968; Manoharan and Rogers 1970; Bernstein and Gray 1972; Sethulakshmi *et al* 1979; Balasivasubramanian *et al* 1982). The four important systems under consideration are $\text{NiX}_2(\text{diphos})_2^+$ and $\text{NiX}_2(\text{diars})_2^+$ where X is chlorine and or bromine. Of the four species, detailed single crystal EPR studies on three of them have already been reported (Bernstein and Gray 1972; Sethulakshmi *et al* 1979; Balasivasubramanian *et al* 1982). The only species left out in this series is $\text{NiBr}_2(\text{diars})_2^+$. The intention of our study on this system is to make a good comparison between the dihalo complexes containing two different bidentate ligands *viz* diphos and diars. A general conclusion based on the single crystal EPR studies on all systems other than $\text{NiBr}_2(\text{diars})_2^+$ reveals that the delocalization of the molecular wavefunction for the unpaired electron of this complex should be most pronounced. This might lead to an enhanced hyperfine interaction with the ligand nuclei. Further it was thought that the effect of this enhanced hyperfine broadening on the shape and width of the single crystal EPR resonance absorption of the pure (undiluted) compound would be very interesting to investigate. In this paper we report the EPR study of $[\text{NiBr}_2(\text{diars})_2]^+\text{Br}^-$ diluted in an isomorphous diamagnetic host lattice $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]\text{Br}$; also, we have made an attempt, in the light of the available theories, to understand the nature and magnitude of the various cooperative magnetic interactions present in the pure solid.

2. Experimental

The trans-dibromobis[*o*-phenylenebisdimethylarsine] nickel(III) bromide $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ was prepared according to the procedure of Nyholm (1950). The

trans-bromonitrosylbis[*o*-phenylenebisdimethylarsine] cobalt(III)] bromide was made following the method of Feltham and Nyholm (1965). Single crystals suitable for EPR measurements were grown by slow evaporation of an alcoholic solution of the cobalt(III) complex containing 1 mol % of nickel(III) complex. Small reddish brown, diamond-shaped crystals of pure $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ were grown from nitromethane solution.

EPR measurements were made at *X*- and *Q*-band frequencies at 300 K using Varian E-112 spectrometer with 100 kHz modulation coils. DPPH was used as a *g*-calibrant. All linewidths reported here are peak-to-peak width of the first derivative spectrum ΔB_{pp} . The error in the linewidth measurements is ± 2 G. However, in the case of diluted crystals it was noticed that nickel(III) has not gone in with adequate concentration in the cobalt(III) lattice. As a result of this poor concentration of Ni(III) in the small crystals of Co(III) complex, the *X*-band spectrum was extremely noisy. Furthermore, the complicated EPR spectra from two different sites with a large number of ligand superhyperfine structure made it almost impossible to make a good analysis of the *X*-band EPR spectral data. Hence all the single crystal EPR measurements on this system were made on the *Q*-band spectrometer.

3. Results and discussion

3.1 EPR of $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ diluted in $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]\text{Br}$

3.1a Crystal structure of $[\text{Fe}(\text{NO})\text{Br}(\text{diars})_2]\text{ClO}_4$: The diamagnetic host lattice chosen for this study viz $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]\text{Br}$ is isomorphous to $[\text{Fe}(\text{NO})\text{Br}(\text{diars})_2]\text{ClO}_4$. The crystal structure of this iron(III) complex has been received by us by a private communication from Professor Dahl. The unit cell is tetragonal with space group $P4/n(C_{4h}^3)$. The lattice parameters are: $a = 17.11 \pm 0.03$ Å, $c = 9.94 \pm 0.02$ Å, $Z = 4$. The cation $\text{Fe}(\text{NO})\text{Br}(\text{diars})_2^+$ is situated in the centre of symmetry. The cation has approximately C_{2v} symmetry, the unique axis being Br–Fe–NO. The projection down the *c* axis is shown in figure 1. The phenylene rings are not coplanar with the FeAs_4 plane, but are inclined. The dihedral angle between the normals to a phenylene ring and FeAs_4 plane was found to be 9° in the iron(III) complex $[\text{Fe}(\text{NO})\text{Br}(\text{diars})_2]\text{ClO}_4$. The average nonbonding Br...CH₃ distance of 3.61 Å is much shorter than the sum of the corresponding van der Waals radii (3.95 Å). Similar distortions do occur in the case of other diars complexes of iron and hence it is possible that such distortions might also occur in the cobalt complex. Silverthorn and Feltham (1967) suggested a nonlinear Fe–N–O bond axis on the basis of their studies on the electronic and infrared spectra. The situation in the cobalt(III) complex cannot be much different from the iron(III) complex because of the isomorphous character. From EPR point of view, there will be two magnetically inequivalent sites when Ni(III) is introduced into the diamagnetic Co(III) lattice. As a result, two sets of Br–Co–NO hence Br–Ni–Br axes will be present which will be mutually perpendicular to each other, one approximately along the *a*- and the other along the *b*-axes.

3.1b *g*-tensor: Though the measurements were done on the three orthogonal planes, 100, 010 and 001, the first two yielded identical spectral data and the angular variation

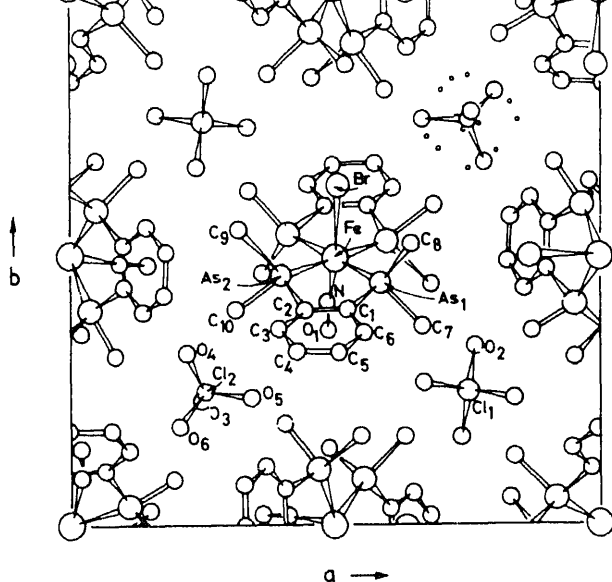


Figure 1. The projection of $[\text{Fe}(\text{NO})\text{Br}(\text{diars})_2]^+$ down the c axis.

parallel either to the a or the b axis, half of the molecules are roughly aligned parallel to the NO-Co-Br axis and hence the Br-Ni-Br axis of the dopant molecule. The remaining half of the molecules will have the bisector of the diars ligand ring parallel to the applied field. Hence the EPR spectrum in such a case is made up of one set of multiplets due to the $g_{\parallel}$ and another set of multiplets due to $g_{\perp}$ as shown in figure 2. The first set of molecules changes on rotation from $g_{\parallel}$ to $g_{\perp}$ and back again to $g_{\parallel}$ during a 180° rotation. However, the g -value of the other set does not change much due to the very small changes in the g -values of the equatorial plane containing the four arsenic atoms. This is quite obvious from figures 3a and 3b.

When c -axis is the rotation axis both sets of molecules move from roughly a $g_{\parallel}$ direction to $g_{\perp}$ direction. It is to be noted that the $g_{\parallel}$ and $g_{\perp}$ sets of lines contain hyperfine splitting due to two Br's and four As's and hence there is considerable overlap between the spectra due to two inequivalent sites except where the g -values have considerable difference. This has led to some complication in identifying the exact position of the g -values. Hence the fitting was done only with the points which we could barely identify.

A least-squares fitting of the g -values was done assuming the direction cosines obtained from crystallographic data given in table 1. There is remarkable similarity between the experimental and calculated points using Br-Ni-Br as the unique axis corresponding to $g_{\parallel}$. The g -anisotropy in the equatorial plane, however minimum, could be identified by this fit. The g -values thus obtained are also given in table 1.

1c *Ligand hyperfine interaction from ^{75}As and $^{79, 81}\text{Br}$:* Since the EPR measurements were made using naturally abundant isotopes of Ni, no metal hyperfine splitting due to ^{60}Ni ($I = 3/2$ with natural abundance of 1.19%) is expected to be clear enough for

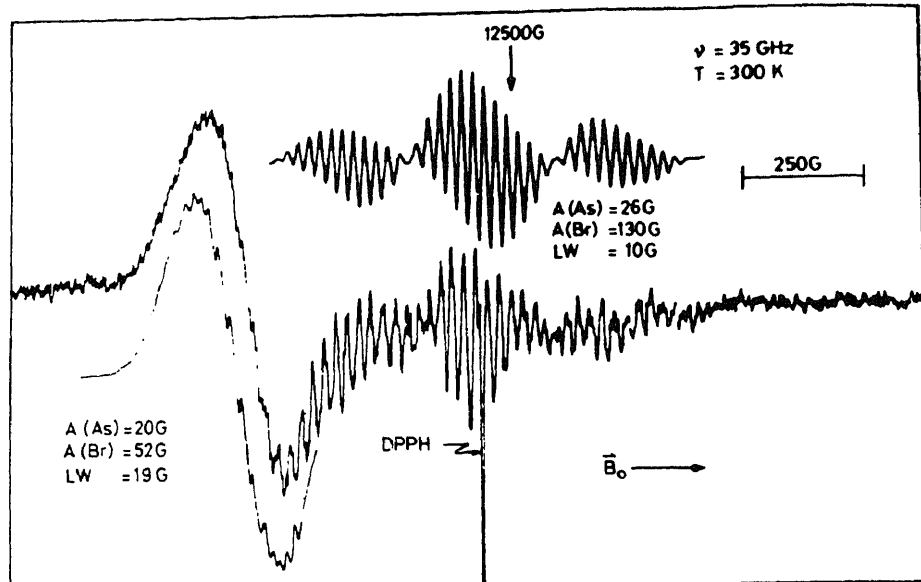


Figure 2. Experimental and simulated single crystal EPR spectra of $[\text{NiBr}_2(\text{diars})_2]^+$ diluted in $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]^+$ at 300 K in the bc plane.

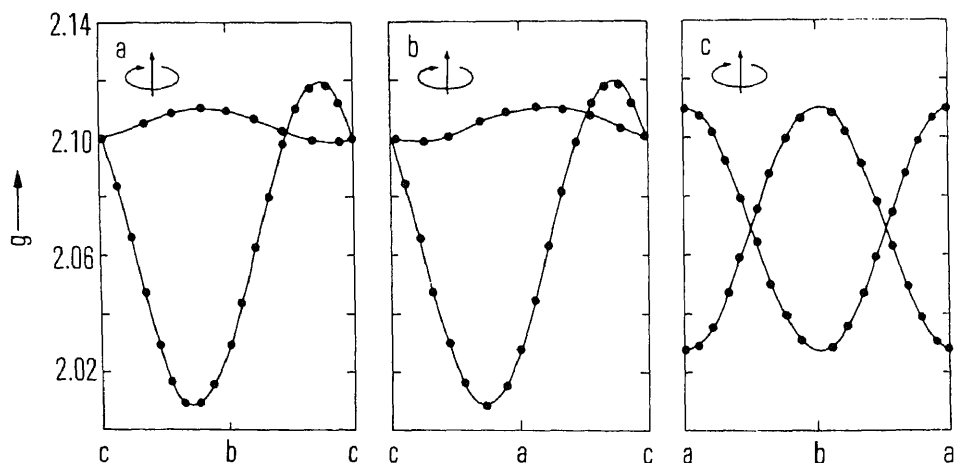


Figure 3. Experimental (●●●) and computed (—) angular variation of g from single crystal Q-band EPR spectra at 300 K in the three orthogonal planes.

detailed analysis. However, it has been found that all the four As atoms and two Br atoms contribute to the multiplet structure. Again because of considerable overlap due to spectra at different orientations we have chosen some of the unique orientations to

Table 1. Principal values of g and ligand hfs tensors for $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ diluted in $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]\text{Br}$ single crystals.

		Direction cosines		
		<i>a</i>	<i>b</i>	<i>c</i>
Site 1	$g_{xx} = 2.120$	-0.239	-0.396	0.887
	$g_{yy} = 2.110$	0.971	-0.125	0.205
	$g_{zz} = 2.008$	0.030	0.910	0.414
Site 2	$g_{xx} = 2.120$	0.396	-0.239	-0.887
	$g_{yy} = 2.110$	0.125	0.971	-0.205
	$g_{zz} = 2.008$	0.910	-0.030	0.41
	$A_{xx}(^{75}\text{As}) = -20 \text{ G}$	$A_{xx}(^{81}\text{Br}) = +52 \text{ G}$		
	$A_{yy}(^{75}\text{As}) = -25 \text{ G}$	$A_{yy}(^{81}\text{Br}) = -46 \text{ G}$		
	$A_{zz}(^{75}\text{As}) = -26 \text{ G}$	$A_{zz}(^{81}\text{Br}) = +130 \text{ G}$		
	$A_{av}(^{75}\text{As}) = -23.7 \text{ G}$	$A_{av}(^{81}\text{Br}) = 45.3 \text{ G}$		
	$A_{iso}(^{75}\text{As}) = 24.7 \text{ G}$	$A_{iso}(^{81}\text{Br}) = 48.5 \text{ G}$		

hyperfine lines due to them has been noticed and hence we report the values corresponding to ^{81}Br .

One of the most characteristic spectrum was obtained when the magnetic field was placed either in the 100 or 010 plane roughly 10° away from either the *b*- or *a*-axis respectively. The experimental spectrum measured along this direction is given in Figure 2. The low-field lines correspond to nearly g_{xx} while the high-field multiplet corresponds to nearly g_{zz} . The simulated spectra corresponding to these g -values are given below and above the experimental spectrum respectively. Similar spectra with little change in the anisotropic values were obtained in another orientation corresponding to g_{yy} and g_{zz} . All the spin hamiltonian parameters for $\text{NiBr}_2(\text{diars})_2^+$ are given in Table 2 and compared with the other dihalo diphos and diars complexes of Ni(III).

It may be noted that hyperfine splitting constants due to ^{75}As is essentially isotropic and the A_{av} of 23.7 G obtained from the present single crystal EPR data compared very well with the A_{iso} of 24.7 G (Manoharan and Rogers 1970). In addition the anisotropic hyperfine splitting constants due to $^{79}, ^{81}\text{Br}$ have been given signs by comparison of the magnitudes of the principal values with that of the isotropic value obtained earlier. The principal values of $A(\text{Br})$ are:

$$A_{xx} = +52 \text{ G},$$

$$A_{yy} = -46 \text{ G},$$

$$A_{zz} = +130 \text{ G},$$

giving an A_{av} of 45.3 G which compares again well with the A_{iso} value of 48.5 G (Manoharan and Rogers 1970).

Electronic structure of $[\text{NiBr}_2(\text{diars})_2]\text{Br}$: With the knowledge of the relative signs of the various hyperfine coupling constants, it would be possible to decipher the electronic structure of the complex ion $[\text{NiBr}_2(\text{diars})_2]^+$ and compare it with other dihalo and diars systems.

Table 2. Spin hamiltonian parameters of $\text{NiX}_2(\text{L-L})_2^+$.

No.	NiX ₂ (L-L) ₂ ⁺	g-tensor values	A-tensor values in gauss			References
			A(L-L)	A(X)		
1.	NiCl ₂ (diphos) ₂ ⁺ L-L = P-P X = Cl	<i>g</i> _{xx} = 2.119 <i>g</i> _{yy} = 2.113 <i>g</i> _{zz} = 2.010	<i>A</i> _{xx} = -13 (1) <i>A</i> _{yy} = -5 (1) <i>A</i> _{zz} = -43.6 (1)	<i>A</i> _{xx} = -15.3 (1) <i>A</i> _{yy} = -18.3 (1) <i>A</i> _{zz} = -17.6 (1)	Sethulakshmi <i>et al</i> (1979)	
2.	NiCl ₂ (diars) ₂ ⁺ L-L = As-As X = Cl	<i>g</i> _{xx} = 2.142 <i>g</i> _{yy} = 2.142 <i>g</i> _{zz} = 2.008	<i>A</i> _{xx} = -8.5 <i>A</i> _{yy} = -6.1 <i>A</i> _{zz} = -32	<i>A</i> _{xx} = -32 <i>A</i> _{yy} = -50 <i>A</i> _{zz} = -29	Bernstein and Gray (1972)	
3.	NiBr ₂ (diphos) ₂ ⁺ L-L = P-P X = Br	<i>g</i> _{xx} = 2.141 <i>g</i> _{yy} = 2.096 <i>g</i> _{zz} = 1.994	<i>A</i> _{xx} = -20 (2) <i>A</i> _{yy} = -20 (2) <i>A</i> _{zz} = -19.4 (1)	<i>A</i> _{xx} = -27 (1) <i>A</i> _{yy} = -61 (1) <i>A</i> _{zz} = -169 (1)	Sethulakshmi <i>et al</i> (1979)	
4.	NiBr ₂ (diars) ₂ ⁺ L-L = As-As X = Br	<i>g</i> _{xx} = 2.120 <i>g</i> _{yy} = 2.110 <i>g</i> _{zz} = 2.008	<i>A</i> _{xx} = -20 (1) <i>A</i> _{yy} = -25 (1) <i>A</i> _{zz} = -26 (1)	<i>A</i> _{xx} = +52 (1) <i>A</i> _{yy} = -46 (1) <i>A</i> _{zz} = +130 (1)	Present work	

positive. The values assigned to the isotropic and the anisotropic hyperfine coupling constants can be used to calculate spin densities on the ligand nuclei and hence the molecular wave function containing the unpaired electron. The isotropic and dipolar coupling constants for the unpaired electron were taken from Ayscough (1967). The experimental spin densities are given in table 3.

The NiBr_2As_4 chromophore may be assigned a D_{2h} symmetry though the correct molecular symmetry in the host lattice could be lower. The only optical transition observed at $14,500\text{ cm}^{-1}$ for this complex in solution can be assigned to ${}^2A_g \rightarrow {}^2B_{2g}$ and ${}^2A_g \rightarrow {}^2B_{3g}$ which are nearly degenerate. Evaluating the g -values to first order by using the relation

$$g_{\perp} = 2.0023 - \frac{6\lambda}{\Delta},$$

where $\lambda = -272\text{ cm}^{-1}$ for Ni(III) , we find $g_{\perp}$ turns out to be 2.115 (observed values are $g_x = 2.120$ and $g_{yy} = 2.110$) and $g_{\parallel}$ is found to be near to that of free spin. Though this includes contribution from ligand spin-orbit coupling, a simple correlation of this kind indicates a d_{z^2} ground state and the correctness of the proposed excited states mentioned above.

The ground state for these ions ${}^2A_g(z^2)$ shall be derived from the electronic configuration

$$[a_g(x^2 - y^2)]^2 < [b_{2g}(xz)]^2 < [b_{3g}(yz)]^2 < [a_g(z^2)]^1 < [b_{1g}(xy)]$$

with the only empty d -orbital being d_{xy} . The LCAO-MO for the unpaired electron can be written (Bernstein and Gray 1972) as

$$a_g(d_{z^2}) = a_1 d_{z^2} + a_2 \phi_{p_z}(\text{Br}) + a_3 \phi_s(\text{As}) - a_4 \phi_{p_x}(\text{As}) - a_5 \phi_{p_z}(\text{As}) - a_6 \phi_s(\text{Br}) - a_7 \phi_{p_x}(\text{Br}), \quad (1)$$

where a_1 and a_2, a_3 etc are metal and ligand orbital coefficients respectively and the ϕ 's are the ligand orbital combinations, defined as

$$\phi_{p_z}(\text{Br}) = 1/\sqrt{2}[p_z(\text{Br}_1) - p_z(\text{Br}_2)]$$

Table 3. Spin densities from ligand hfs tensor for $[\text{NiBr}(\text{diars})_2]\text{Br}$ doped $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]\text{Br}$ single crystals.

	A (gauss)	ρ (%)
${}^{75}\text{As}$	$A_{\text{iso}} = -23.67$	$\rho_{4s} = 0.69$
	$A_{\text{dip major}} = 4.00$	$\rho_{4p\sigma} = 2.19$
	$A_{\text{dip minor}} = 0.66$	$\rho_{4p\pi} = 0.36$
	$A_{\text{iso}} = 45.17$	$\rho_{4s} = 0.54$
${}^{81}\text{Br}$	$A_{\text{dip major}} = 117.67$	$\rho_{4p\sigma} = 20.86$
	$A_{\text{dip minor}} = 52.00$	$\rho_{4p\pi} = 9.22$
		$\rho_{(\text{As})} = 12.96$
		$\rho_{(\text{Br})} = 61.24$
		$\rho_{(\text{ligand})} = 74$

$$\begin{aligned}\phi_s(\text{As}) &= (1/\sqrt{2}) [s(\text{As}_1) + s(\text{As}_2) + s(\text{As}_3) + s(\text{As}_4)] \\ \phi_{p_e}(\text{As}) &= (1/2) [p_x(\text{As}_1) - p_x(\text{As}_2) + p_x(\text{As}_3) + p_x(\text{As}_4)] \\ \phi_{p_x}(\text{As}) &= (1/2) [p_y(\text{As}_1) + p_y(\text{As}_2) - p_y(\text{As}_3) - p_y(\text{As}_4)] \\ \phi_s(\text{Br}) &= (1/\sqrt{2}) [s(\text{Br}_1) + s(\text{Br}_2)], \\ \phi_{p_x}(\text{Br}) &= (1/\sqrt{2}) [p_x(\text{Br}_1) - p_x(\text{Br}_2)].\end{aligned}$$

The ligand orbital coefficients are directly obtained from the spin-density data given in table 3. The total unpaired electron density on the ligand turns out to be 74 %. Imposing the normalization condition on equation (1), we get

$$\int |\psi(d_{z^2})|^2 d\tau = a_1^2 + \sum_{j=2}^7 a_j^2 + 2a_1 \sum_{j=2}^7 a_j S_{ij} = 1, \quad (3)$$

Where S_{ij} 's are the overlap integrals evaluated by using Richardson's functions (Richardson *et al* 1962) for the metal atom and Clementi's functions (Clementi 1965) for the ligands. Using equation (3) and a_j 's we obtain the metal-orbital coefficient a_1 . The overlap integrals and the MO coefficients are listed in table 4. Comparison of these coefficients with those for the other diars and diphos complexes of Ni(III) (table 5), gives an idea of the quantitative changes in the modes of bonding as we go from P to As in Group VB and from Cl to Br in group VII B.

The EPR results of $[\text{NiBr}_2(\text{diars})_2]^+$ together with the results reported earlier show considerable delocalization of the unpaired spin density. Ligand hyperfine tensors and an approximate LCAO-MO approach show an increase of covalency in the order $[\text{NiCl}_2(\text{diphos})_2]^+ < [\text{NiCl}_2(\text{diars})_2]^+ < [\text{NiBr}_2(\text{diars})_2]^+ < [\text{NiBr}_2(\text{diphos})_2]^+$ in slight disagreement with our earlier predictions (Sethulakshmi *et al* 1979). It is worthwhile to mention here that some of the errors due to improper normalisation of the wavefunctions in the earlier works have now been corrected. A comparison indicates that the total unpaired spin density in the ligands increases in the same order

$$\begin{aligned}\text{NiCl}_2(\text{diphos})_2^+ (68.6\%) &< \text{NiCl}_2(\text{diars})_2^+ (76.8\%), \\ &< \text{NiBr}_2(\text{diars})_2^+ (74\%) < \text{NiBr}_2(\text{diphos})_2^+ (86.1\%).\end{aligned}$$

In the bromo complexes, there is considerable σ delocalization onto the axial bromines, leading to a net higher covalency. It is striking that the covalency increases whenever the

Table 4. Overlap integrals and molecular orbital coefficients for $[\text{NiBr}_2(\text{diars})_2]\text{Br}$.

Atomic orbitals	a_j	Group overlap integrals S_{ij}
$\phi_{p_x}(\text{Br})$	0.45672	0.06713
$s(\text{As})$	0.08307	0.09524
$p_\sigma(\text{As})$	0.14799	0.12883
$p_x(\text{As})$	0.06000	0
$s(\text{Br})$	0.07349	0.04066
$p_x(\text{Br})$	0.30365	0

Table 5. Molecular orbital coefficients and overlap integrals for a series of dihalo diphos and diars complexes of low-spin d^7 Ni(III).

A.O's	[NiCl ₂ (diphos) ₂] ⁺ L = P X = Cl			[NiBr ₂ (diphos) ₂] ⁺ L = P X = Br			[NiCl ₂ (diars) ₂] ⁺ L = As X = Cl			[NiBr ₂ (diars) ₂] ⁺ L = As X = Br		
	<i>a_j</i>	<i>S_{ij}</i>		<i>a_j</i>	<i>S_{ij}</i>		<i>a_j</i>	<i>S_{ij}</i>		<i>a_j</i>	<i>S_{ij}</i>	
<i>p_z</i> (X)	0.1414	0.0742		0.4123	0.0671		0.3742	0.0742		0.4567	0.0671	
<i>s</i> (L)	0.0775	0.1030		0.0775	0.1030		0.0678	0.0952		0.0831	0.0952	
<i>p_z</i> (L)	0.3507	0.1378		0.0227	0.1373		0.3017	0.1288		0.1480	0.1288	
<i>p_x</i> (L)	0.1581	0		0.0227	0		0.0707	0		0.06	0	
<i>s</i> (X)	0.1	0.0482		0.1	0.0407		0.1414	0.0482		0.0735	0.0407	
<i>p_x</i> (X)	0.0707	0		0.2074	0		0.1483	0		0.3036	0	
<i>d_{z²}</i> (Ni)	0.9359	—		0.8495	—		0.8585	—		0.7969	—	

4s and 4p orbitals are involved. This must be due to the extended radial part of the wave functions of 4s and 4p orbitals. In $[\text{NiCl}_2(\text{diphos})_2]^+$, the unpaired electron is least delocalized onto the ligands in this series since both phosphorous and chlorine orbitals involved in the MO formation are of the 3s and 3p type.

3.2 EPR of pure $[\text{NiBr}_2(\text{diars})_2]\text{Br}$

$[\text{NiBr}_2(\text{diars})_2]\text{Br}$ is isomorphous to $[\text{NiCl}_2(\text{diars})_2]\text{Cl}$ whose crystal structure is known (Berstein *et al* 1972). The crystal is monoclinic with two molecules per unit cell and the differences in their orientations are clear from figure 4 where the projection in the ac^* plane is shown.

3.2a g -Tensor. The principal g -values for $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ obtained by a diagonalisation procedure, agree very closely with the powder g -values reported by Manoharan and Rogers (1970). A single line was observed at all orientations at both X - and Q -band frequencies, which clearly indicates that there is exchange between the two sites and that it is stronger than one half of the separation between them even at Q -band. To confirm this, we have calculated the average g -tensor from the two molecular g -tensors by taking their relative orientations (Mooij *et al* 1976). The principal g -values thus calculated are in reasonable agreement with experimental values. The direction cosines, however, differ to a greater extent than experimental values. All the values are listed in table 6 for comparison.

The angular variation of g was simulated in the ac^* plane (where the two sites are

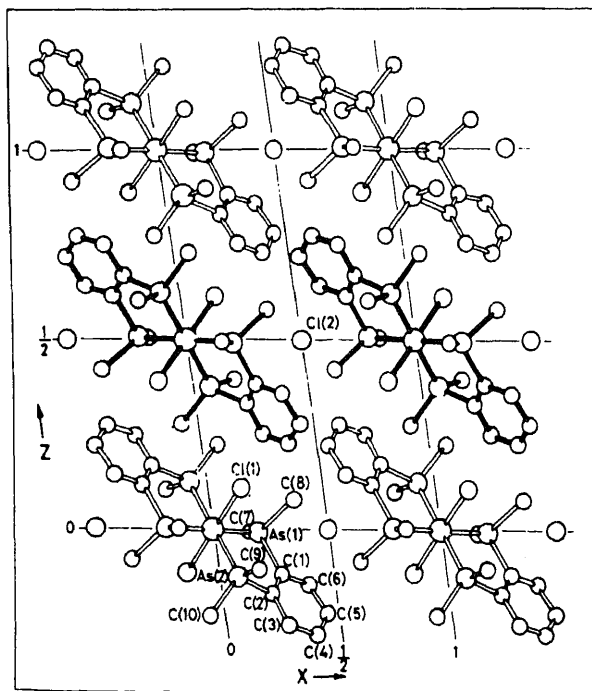


Table 6. Spin hamiltonian parameters^a for [NiBr₂(diars)₂]Br.

<i>g</i> -tensor directions	Doped single crystal	Pure powder	Pure single crystal	Average <i>g</i> -tensor calculated
<i>g_{xx}</i>	2.120	2.119	2.119	2.120
<i>g_{yy}</i>	2.110	2.069	2.068	2.075
<i>g_{zz}</i>	2.008	2.043	2.043	2.044

	Direction cosines ^b for <i>g_{av}</i> (calculated)			Direction cosines ^c for pure crystal		
	<i>a</i>	<i>b</i>	<i>c</i> *	<i>a</i>	<i>b</i>	<i>c</i> *
<i>g_{xx}</i>	0.795	0	-0.606	0.702	0.185	-0.688
<i>g_{yy}</i>	0	1	0	0.283	0.920	0.273
<i>g_{zz}</i>	0.606	0	0.795	0.686	0.207	0.698

^a*g*-value are accurate upto ±0.001.^b Calculated using the direction cosines of the two sites obtained from the crystal structure.^c Obtained by the diagonalisation of the experimental values.

equivalent throughout and hence no effect of exchange is felt on the *g*-value) using the principal values from the doped case and the direction cosines from the crystal structure. The fit with the experimental variation is remarkable and is shown in figure 5a. This proves that the rhombic nature of the *g*-tensor arises not because of any change in the ground state but due to exchange averaging between magnetically inequivalent sites. Such an averaging of the *g*-tensor has been noticed in several other systems (Manoharan *et al* 1981; Ramakrishna and Manoharan 1984).

3.2b Line width: To get an idea of the variety of strength of the interactions, the line width was measured at *X*- and *Q*-band and frequencies in the *ab*, *bc* and *ac** planes. The understanding of the variation in the *ac** plane (where two sites are magnetically equivalent) is somewhat easier and hence is considered first.

The line shape analysis revealed that the line in *ac** plane is almost Lorentzian in character (figure 6) and this indicates that exchange is much stronger than any of the broadening mechanisms—dipolar or hyperfine.

A range of values of 700 G to 1000 G for the exchange parameter *J*₀, is obtained from the relation given by Van Vleck (1948) for strong exchange narrowing case

$$\Delta B_{pp} = \frac{2}{\sqrt{3}} \frac{M_2^{\text{total}}}{J_0} \quad (4)$$

where *M*₂ total is the total secular second moment from both the dipolar and hyperfine contributions and using ΔB_{pp} obtained from *Q*-band spectra.

The angular variation of the *X*- and *Q*-band line widths in the *ac** plane is shown in figure 5b. The fact that *Q*-band line widths are always smaller indicates that we are in a *J*-regime where secular and non-secular contributions to the line width are quite important. The fact that the *Q*-band line widths are smaller than the *X*-band line widths is due to the non-secular parts becoming more

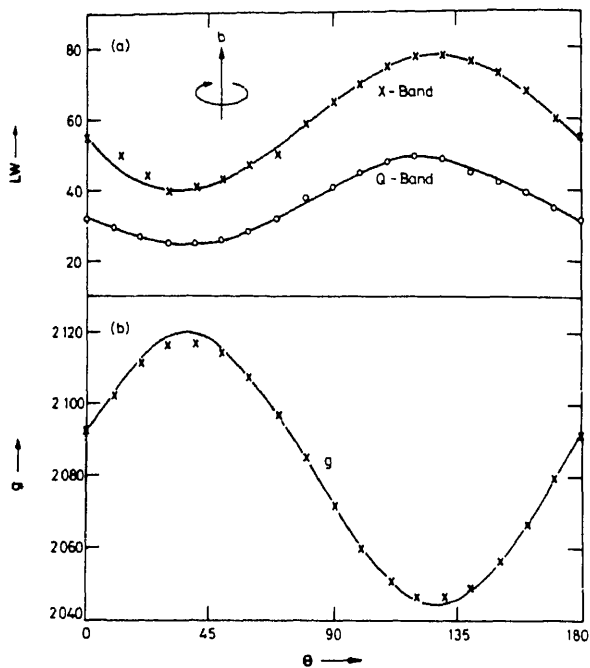


Figure 5. (a) Angular variation of line width in X- and Q-band spectra. (b) g -simulation for pure $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ in the ac^* plane at 300 K.

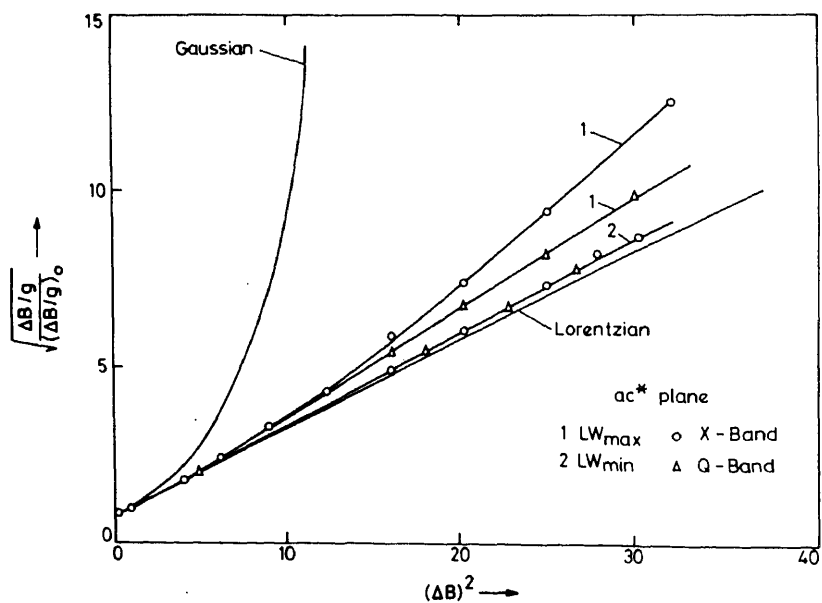


Table 7. Local fields and $\Delta B_X - \Delta B_Q$ for $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ in ac^* plane from single crystal EPR results at 300 K.

Angle ($^\circ$) B_0 with axis	Dipolar ^a Second moments $\times 10^{-3} \text{ G}^2$			Hyperfine ^b Second moments $\times 10^{-3} \text{ G}^2$		$\Delta B_X - \Delta B_Q$ (gauss)
	$\Delta m = 0$	$\Delta m = \pm 1$	$\Delta m = \pm 2$	Secular	Non-secular	
	1.55	6.05	1.94	6.90	14.60	28
	1.86	5.72	1.91	10.52	13.73	27
	2.79	4.54	1.95	18.19	11.87	24
0	2.49	4.63	1.89	26.06	9.92	21
0	1.51	5.51	1.79	30.63	8.79	17

^a In calculating dipolar interaction the point-dipole has been resorted to.

^b 5–10% increase is expected if the spin-delocalization is taken into account.

^c Axially symmetry g - and A -tensors were assumed.

^d Tensor values used are: $A_{\parallel}(\text{As}) = 26 \text{ G}$ $A_{\parallel}(\text{Br}) = 130 \text{ G}$ $A_{\perp}(\text{As}) = 22 \text{ G}$ $A_{\perp}(\text{Br}) = 50 \text{ G}$.

We have used the method of Soos *et al* (1973) to obtain the fourier components of the spin correlation functions from the angular and frequency variation of line width for $\Gamma \gg J$ with the knowledge of local fields. The method is useful when the sites become magnetically equivalent (which is true for $\text{NiBr}_2(\text{diars})_2^+$ in the ac^* plane) and provides a direct test for the various theoretical models (Blume and Hubbard 1970; Anderson and Weiss 1953) of spin correlation functions. The angular dependence of the local field amplitudes computed *via* the second moments along with the experimental $\Delta B_X - \Delta B_Q$ values at X - and Q -bands are summarised in table 7.

The total ΔB_{pp} is given by

$$\begin{aligned} \frac{\sqrt{3}}{2} \Delta B_{\text{pp}} &= \Gamma_{\text{total}} \\ &= \Gamma_{\text{dipolar}} + \Gamma_{\text{hyperfine}} \\ &= M_2^{(0)} f(0) + M_2^{(1)} f(\omega_0) + M_2^{(2)} f(2\omega_0) + a^{(0)} g(0) + a^{(1)} g(\omega_0) \end{aligned} \quad (5)$$

where $g(\omega)$ is the fourier component of the autocorrelation function $C(t)$, and $f(\omega)$ is the Fourier component of $C^2(t)$. The Fourier components describe the time evolution due solely to the exchange hamiltonian and are independent of orientation in the strong coupling limit. Thus the angular variation of linewidth provides enough equations to evaluate all the five unknowns.

2c Nonsecular spin correlations: The nonsecular ($\omega \neq 0$) correlations have been calculated as was done by Soos *et al* (1973) by relating the difference between the X - and Q -band linewidths. The equations for various orientations are

$$\begin{aligned} \frac{\sqrt{3}}{2} [\Delta B_X(\theta, \phi) - \Delta B_Q(\theta, \phi)] &= M_2^{(1)}(\theta, \phi) \Delta f(\omega) \\ &\quad + M_2^{(2)}(\theta, \phi) \Delta f(2\omega) + a^{(1)} \Delta g(\omega), \end{aligned} \quad (6)$$

where $M_2^{(1)}$ and $M_2^{(2)}$ are the nonsecular dipolar second moments corresponding to Δm

components at Larmor frequency, $\Delta f(2\omega)$ is the difference at twice the Larmor frequency and $\Delta g(\omega)$ is the corresponding difference for the hyperfine Fourier component. By solving (6) by least squares procedure we have obtained

$$\begin{aligned}g(\omega) &= 0.152 \times 10^{-3} \text{G}^{-1}, \\f(\omega) &= 2.68 \times 10^{-3} \text{G}^{-1}, \\f(2\omega) &= 1.25 \times 10^{-3} \text{G}^{-1}.\end{aligned}$$

Using the $B-H$ and $A-W$ form for $C(t)$, the calculated values of the Fourier components were found to be smaller than the above mentioned experimental ones. This coupled with the fact that the angular dependence of the '10/3 effect' is not very well reproduced by the above Fourier components suggests that we are in a regime where the approximations involved in the above theories are not quite valid. Also very different spin correlation functions may contribute to different orientations of the Zeeman field.

3.2d Secular spin correlations: Using the nonsecular Fourier components obtained, we tried to evaluate $g(0)$ and $f(0)$ by fitting the total linewidth. Unique positive values for either $g(0)$ or $f(0)$ could not be obtained by solving (5) which clearly shows that these secular Fourier components are sensitive to orientation of the magnetic field **B**.

3.2e Ratio method: We have tried a more qualitative type of analysis which just uses the Kubo-Tomita (1954) theory to evaluate the exchange field by the ratio of the line width at two observation frequencies. The linewidth at any Zeeman frequency assuming a Gaussian correlation function is given by

$$\Delta\omega_{1/2} = (\pi/2)^{1/2} \left[\frac{M_2^{(0)}}{\omega_{e0}} + \frac{M_2^{(1)}}{\omega_{e1}} \exp\left(-\frac{\omega_{zee}^2}{2\omega_{e1}^2}\right) + \frac{M_2^{(2)}}{\omega_{e2}} \exp\left(-\frac{2\omega_{zee}^2}{\omega_{e2}^2}\right) \right], \quad (7)$$

where $M_2^{(0)}$ is the secular ($\Delta m = 0$) dipolar second moment and ω_{er} ($r = 0, 1, 2$) are the exchange parameters for the different contributions, all taken to be equal to ω_0 in the large exchange limit. From the linewidth studies at two observation frequencies at X - and Q -bands, the ratio $\Delta B_X/\Delta B_Q$ can be measured and using $M_2^{(r)}$ from crystal structure, one can evaluate ω_0 .

Assuming $\omega_{e0} = \omega_{e1} = \omega_{e2} = \omega_e$, the ratios obtained at five orientations were used to evaluate the exchange parameter. The ratio at two Zeeman frequencies can be fitted to two values of exchange and a plot of the ratio $\Delta B_X/\Delta B_Q$ as a function of frequency for a particular orientation in ac^* plane is shown in figure 7. Only one value of the exchange frequency which is physically meaningful is chosen. Pleau and Kokoszka (1973) used the method of ratios effectively and the frequency obtained can be related to J in the high temperature approximation by an equation of Moriya (1956).

$$\hbar^2 \omega_e^2 = \frac{8}{3} J^2 z S(S+1), \quad (8)$$

where z is the number of neighbouring spins in the lattice. The ω_e value for

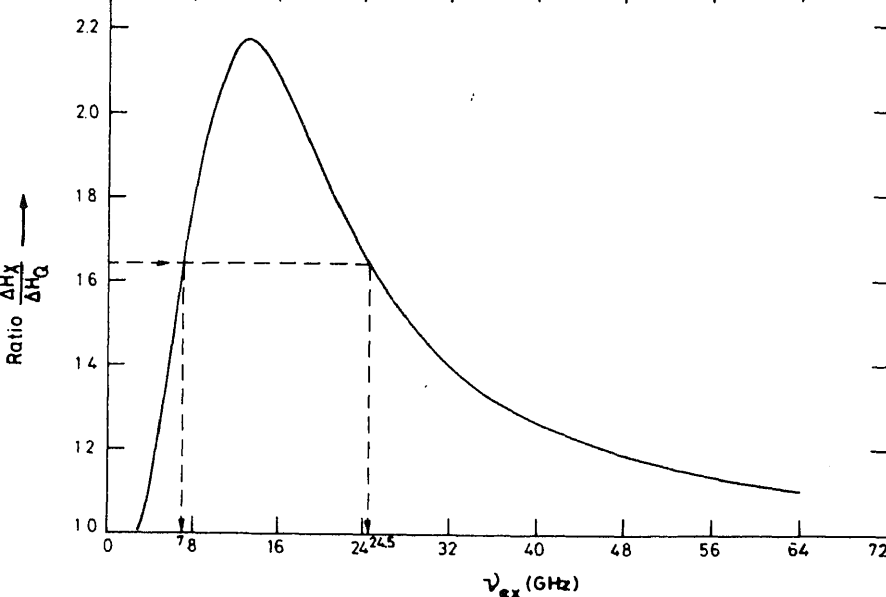


Figure 7. $\Delta B_X/\Delta B_Q$ ratio plotted against frequency for an arbitrary orientations in the ac^* plane.

bc^* plane without any exchange). The angular variation of g for the two sites in the plane (without exchange) is shown in figure 8a. The intersite exchange parameter J' can be evaluated by the ΔB_{pp} variation in a plane where the two sites are magnetically equivalent by measuring at X - and Q -band frequencies. The lines in the ab plane were early Lorentzian both in X - and in Q -band frequencies and hence the strong exchange theory is also applicable here.

Theories of exchange narrowing predict that the frequency dependent line width due to inequivalent sites (Yokota and Koide 1954; Hughes *et al* 1975) depends on the square of the splitting, ΔB_Q or ΔB_X , which ought to have been but for exchange,

$$\Delta B_{pp}(Q) - \Delta B_{pp}(X) = \frac{\Delta B_Q^2 - \Delta B_X^2}{B_e}, \quad (9)$$

where B_e is given by

$$(g\beta/h)B_e = 4t_c^{-1}(\sqrt{3}/2), \quad (10)$$

where t_c is a correlation time given by Hughes *et al* (1975) as

$$t_c = 0.16 \text{ h} |J|^{1/3} / |J'|^{4/3}. \quad (11)$$

The quantity B_e depends on the rate of exchange between the inequivalent sites. For large values of exchange, the Q -band line widths are always larger than the X -band line widths because the secular and nonsecular Fourier components are not frequency-dependent. But in this case as the value of exchange is rather small, the Q -band line width is smaller than the X -band line width at certain orientations are revealed by

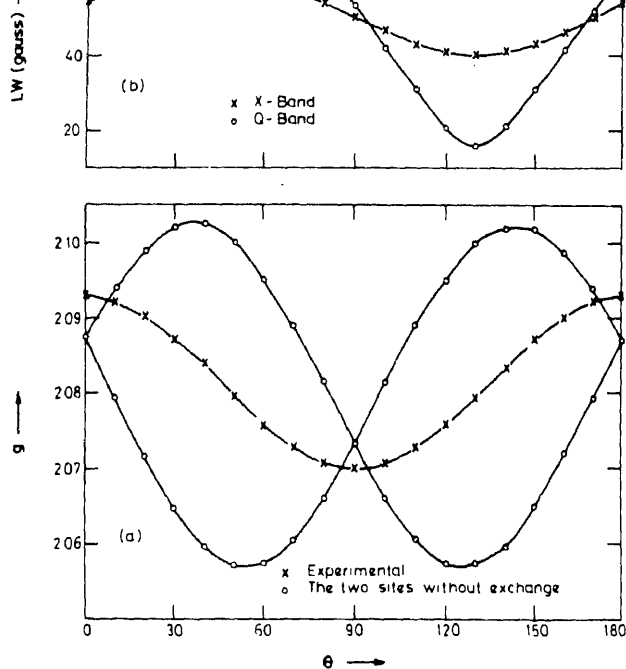


Figure 8. (a) Angular variation of g of the two sites in the ab plane without exchange (OOO) together with the observed g -variation of the single exchange narrowed line ($\times \times \times$). (b) The angular variation of line width in the ab plane at X-band ($\times \times \times$) and Q-band (OOO) at 300 K.

figure 8b. The value of B_e has been obtained to be 2000 G from the angular variation of the line width even though only one angle is sufficient.

The intersite exchange parameter J' was found to be 380 G assuming a value of 800 G for J . This shows that J' is of the same order as J and hence that $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ like its chloro analogue (Ramakrishna and Manoharan, 1984) is close to a 3-d system. However, one cannot take the actual value of J' too literally as the formalism used above to calculate its value involves certain assumptions (Hughes *et al* 1975) which are not quite applicable to $[\text{NiBr}_2(\text{diars})_2]\text{Br}$. Also such a small ratio of intrasite to intersite coupling makes the strong decoupling approximation used earlier for the dipolar four-spin correlation suspect.

4. Conclusion

The EPR spectra of $[\text{NiBr}_2(\text{diars})_2]^+\text{Br}^-$ diluted in the tetragonal host lattice $[\text{Co}(\text{NO})\text{Br}(\text{diars})_2]^+\text{Br}^-$ show that there are two magnetically inequivalent sites with a very large bromine hyperfine splitting. The experimental g ligand hyperfine splittings

there is extensive delocalization over all the ligand nuclei due to the extended 4s and 4p radial wavefunctions.

Also, the EPR study of pure, paramagnetic complex $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ indicates an averaging of the g -tensor due to weak exchange (800 G) and hence only a single line at all orientations at both X - and Q -band frequencies. This exchange averaging is the cause for the g -tensor variation with concentration. The basically Lorentzian line shape atleast near the centre implies that the value of exchange is much larger than the broadening mechanisms.

Neither the A-W model nor the B-H model could predict the Fourier components of the spin correlation function accurately and the values obtained were consistently lower than the ones determined by the study of the angular variation of the '10/3 effect'. The more qualitative Van Vleck procedure yields a value of 800 G for the exchange parameter and this agrees reasonably with the ratio method using the Kubo-Tomita model and Gaussian correlation function. We have estimated the intersite coupling to be 380 G which indicates that $[\text{NiBr}_2(\text{diars})_2]\text{Br}$ is close to a 3-d system.

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Electron spin resonance studies of distorted octahedral ruthenium(III) species

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Abstract. The g -tensor theory of low-spin d^5 configuration in octahedral fields having axial (tetragonal or trigonal) and rhombic distortions is summarised. Illustrations taken from literature concern the following ruthenium(III) species: $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ (trigonal), $\text{Ru}(\text{bpy})_3^{3+}$ (trigonal), the Creutz-Taube cation (axial + rhombic) and $\text{RuCl}_2(\text{HL})$ (L) (axial + rhombic; HL = isonitrosoketone). The rationalisation of distortion parameters in terms of bonding is considered.

Keywords. Ruthenium; distortion parameters; electron spin resonance.

1. Introduction

Electron spin resonance studies of low-spin d^5 ions in grossly octahedral environments were initiated nearly three decades ago and it has continued to be an area of significant activity through the years. One reason for this is no doubt the widespread interest in the compounds of iron(III) and ruthenium(III) which span the d^5 configuration. Historically the first-ever observation of ligand hyperfine in ESR was made by Owen and Stevens (1953) in the low-spin d^5 ion IrCl_6^{2-} . Significant distortion from cubic symmetry were noted by Baker *et al* (1956) and Bleaney and O'Brien (1956) in $\text{Fe}(\text{CN})_6^{3-}$ —an ion often considered to be ideally octahedral. The evaluation of the nature and extent of the subtle distortions of grossly octahedral environments has indeed been a focal point in ESR studies of low-spin d^5 ions.

In this article we examine the ESR parameters of a few pseudooctahedral ruthenium(III) complexes after briefly overviewing the theory of low-spin d^5 g -tensors. It is more of a short personal account of an area where our interest has grown in recent years.

2. Theory

In octahedral geometry, the 2T_2 ground term for low-spin d^5 species arises from the configuration t_2^5 (contributions from excited states are ignored for the present). The g -tensor theory of this configuration was developed by Bleaney and O'Brien (1956) and by Griffith (1961) in the framework of hole formalism. We shall follow the direct five-electron approach of Hill (1972) in a modified form.

A general distortion of the octahedron is expressed as the sum of axial and rhombic distortion. The axial distortion which can be tetragonal (or trigonal) splits the one-

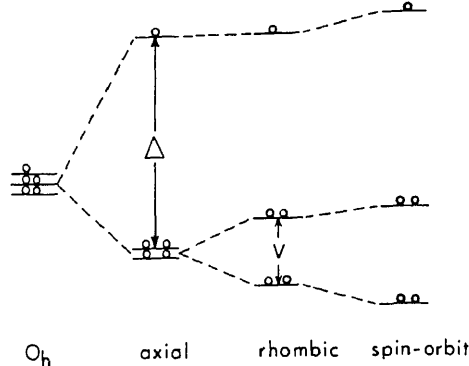


Figure 1. Splitting of t_2 level due to distortions and spin-orbit coupling.

electron t_2 representation into **b** (or **a**) and **e** representations (small letters are used for one-electron representations and capital letters for state representations). The rhombic component splits **e** further into two nondegenerate orbitals. This is illustrated in figure 1. The axial splitting parameter Δ is defined to be positive when **b** (or **a**) lies above **e** as in figure 1. In the d^5 system the spin-orbit coupling parameter (λ) is positive.

The three one-electron t_2 functions can be constructed from the spherical harmonics Y_2^m (Sugano *et al* 1970) in a manner compatible with the anticipated distortion. The six five-electron functions corresponding to the 2T_2 state are obtained by populating these base functions. In tetragonal (or trigonal) symmetry the states span the representations *B* (or *A*), and *E* (consisting of E_+ and E_-) each with either α or β spin. For Δ positive, the configuration e^4b^1 (or e^4a^1) is lower in energy than e^3b^2 (or e^3a^2) and consequently the nondegenerate state *B* (or *A*) lies lower than *E*. The case *E* below *B* (or *A*) corresponds to negative Δ . In the presence of rhombic distortion, the *E* representation is no longer appropriate. However we shall continue to use the E_+ and E_- labels even in rhombic cases to stress the parenthood of the states so labelled.

For visualisation, the one-electron base functions of table 1 can be combined to afford the *d*-orbitals in familiar real forms. In a tetragonal system with *z* as the tetragonal axis, d_{xy} lies above d_{xz} , d_{yz} when Δ is positive and d_{yz} lies above d_{xz} when the added rhombic splitting V is positive. In a trigonal system (*z* is the trigonal axis here) Δ is positive when d_{z^2} lies highest. The two other orbitals are respectively linear

Table 1. The t_2 functions in tetragonal and trigonal situations.

Function		
Tetragonal	Trigonal	Representation
$\frac{1}{\sqrt{2}}(Y_2^0 - Y_2^{-2})$	Y_2^0	b(a)
Y_2^{-1}	$-(\sqrt{2}Y_2^{-2} + Y_2^1)/\sqrt{3}$	e₊
$-Y_2^1$	$(\sqrt{2}Y_2^1 - Y_2^{-1})/\sqrt{3}$	e₋

Table 2. The energy matrix.

		$ E_- \rangle$ $ \bar{E}_+ \rangle$	$ \bar{B} \text{ (or } \bar{A}) \rangle$ $ B \text{ (or } A) \rangle$	$ E_+ \rangle$ $ \bar{E}_- \rangle$
$ E_- \rangle$ $ \bar{B} \text{ (or } \bar{A}) \rangle$	$ \bar{E}_+ \rangle$ $ B \text{ (or } A) \rangle$	$2\Delta + \lambda/2$ 0	0 Δ	$V/2$ $-\lambda/\sqrt{2}$
$ E_+ \rangle$ $ \bar{E}_- \rangle$	$ \bar{E}_- \rangle$ $ \bar{E}_+ \rangle$	$V/2$ $-\lambda/\sqrt{2}$	$-\lambda/\sqrt{2}$ $2\Delta - \lambda/2$	$2\Delta - \lambda/2$ $2\Delta - \lambda/2$

combinations of $d_{x^2-y^2}$ with d_{xz} and d_{xy} with d_{yz} and for positive V the former lies above the latter.

Under the combined effects of Δ , V and λ the six 2T_2 functions split into three Kramers doublets represented by two identical 3×3 matrices, as shown in table 2. States with β -spin are identified by putting a bar on top. The form of the matrix in table 2 is independent of the precise nature of the distortion.

The ground Kramers doublet is in equation (1) where the coefficients a , b and c (not to be confused with symmetry labels **a** and **b** of one-electron

$$\psi_1 = a|E_+ \rangle + b|\bar{B} \text{ or } \bar{A} \rangle + c|E_- \rangle, \quad (1a)$$

$$\psi_2 = a|\bar{E}_- \rangle + b|B \text{ or } A \rangle + c|\bar{E}_+ \rangle, \quad (1b)$$

orbitals used earlier) are real and depend on Δ , V and λ . In strict octahedral symmetry $a = \sqrt{2/3}$, $b = \sqrt{1/3}$ and $c = 0$. The three components of the g -tensor arise as matrix elements of $\beta H(2S + kL)$ within the two states and are stated in equations (2a)–(2c), where k is the orbital

$$g_x = 2[-2ac - b^2 - \sqrt{2}kb(a+c)], \quad (2a)$$

$$g_y = 2[2ac - b^2 - \sqrt{2}kb(a-c)], \quad (2b)$$

$$g_z = 2[-a^2 + b^2 - c^2 - k(a^2 - c^2)], \quad (2c)$$

$$a^2 + b^2 + c^2 = 1, \quad (3)$$

reduction factor assumed to be isotropic. The normalization condition for coefficients in equation (3). Changing the signs of any two of the equations among (2a)–(2c) corresponds to a mere rotation by π radian around an axis and leaves the physical results unaffected (Abragam and Bleaney 1970). The signs as chosen in equations (2a)–(2c) afford identical (in sign and magnitude) g_x and g_y in the axial case ($c = 0$).

The true orbital reduction factor should necessarily be less than 1. The actual value of k derived from experimental results with the help of (2)–(3) is often > 1 due to the presence of unaccounted effects. One of these effects is the admixture of the t_2^5 configuration with the excited configuration $t_2^4 e$ as shown by Thornley (1968) and Griffith (1971). Hill (1972) and Cotton (1972) have shown that this admixture can be accounted for by replacing k of (2) by the factor K as given by (4) where B is the Racah parameter and E_{av} is the average excitation energy of the $t_2^4 e$ configuration. In addition k should be replaced by Λ as defined in (5).

$$K = (1 + 12B/E_{av})k, \quad (4)$$

$K \sim 1.24 k$ and $\Lambda \sim \lambda$. Too much significance should not be attached to the values of k as indices of electron delocalisation.

3. Data processing

Given the signs and magnitudes of g_x , g_y and g_z , the parameters a , b , c , k , Δ/λ , V/λ as well as Kramers doublet eigenfunctions and eigenvalues can be found with the help of equations (2)–(4) and the matrix of table 2. In practice, the ESR experiment provides only the magnitudes of the three principal g values (g_1 , g_2 and g_3). Neither their sign nor their correspondence to g_x , g_y and g_z are known. There are therefore fortyeight possible combinations. Some of these are physically equivalent. Thus by permuting g_1 , g_2 and g_3 in the slots of g_x , g_y and g_z having fixed signs, a set of six correspondences can be generated which differ in some or all of the parameters a , b , c , Δ/λ and V/λ but which are physically equivalent and have the same value of k and relative energies of the Kramers doublets. The fortyeight possible combinations are aggregates of eight such sets each having six combinations. Hence by the choice of a suitable axes system and a correspondence (this is easily achieved in single crystal work with substances of known crystal structure) between g_1 , g_2 , g_3 and g_x , g_y , g_z (say, $g_1 = g_x$, $g_2 = g_y$ and $g_3 = g_z$) only eight alternatives differing in the signs of one or more g 's remain to be considered. Not all of these are physically meaningful and the value of K is often used as the criterion of acceptability. In most cases one is left to choose one from two alternatives which differ in the sign of one of the three g 's. Relatively simple programmes (Hudson and Kennedy 1969; Sakaki *et al* 1978) can be devised to compute upto this stage. The final choice is usually made by considering several factors including the sign and magnitude of Δ . The most powerful discriminator is, however, the energetics of the optical transitions from the ground Kramers doublet to the excited ones ($\Delta E_1/\lambda$ and $\Delta E_2/\lambda$). Unfortunately such transitions are not always observable.

4. Examples

In the following sections we examine the ESR data of four pseudo-octahedral ruthenium(III) species in terms of distortion and other parameters discussed above. The chemical importance of the species chosen is delineated in each case. Trigonal and tetragonal situations are considered. The ESR g -values have been taken from the literature. Since different authors often process their data using different formalisms and sign conventions for parameters, we have, for the sake of consistency, reprocessed all data in terms of equations (2)–(4) and the matrix of table 2. Our discussion is based on parameters so derived.

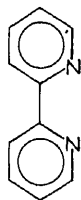
4.1 Hexaaquoruthenium(III) cation, $\text{Ru}(\text{H}_2\text{O})_6^{3+}$

Well-characterised aquo ions of $4d$ and $5d$ elements are sparse in sharp contrast to those of the $3d$ metals. The low-spin $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ ions is thus of special interest. Bernhard *et al* (1984) has reported both single crystal and powdered ESR spectra of the cation doped into the alum $\text{CsGa}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The alum has a β -type structure (Beattie *et al* 1981) with the $\text{M}(\text{H}_2\text{O})_6^{3+}$ octahedra showing a small trigonal distortion along the crystallographic $[111]$ axis.

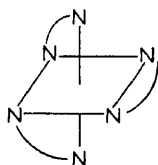
primarily reflects the axial distortion: $|g_z| = |g_{||}| = 1.489$ and $|g_x| = |g_y| = |g_{\perp}| = 2.514$. From the angular dependence of the g values of a rotated crystal it is concluded that the g axis coincides with the $[111]$ crystal axis. The hyperfine coupling of the electron spin with the ^{101}Ru nucleus ($I = 5/2$) produces six equally spaced lines in the $g_{||}$ region with $|A_{||}| = 2 \times 10^{-3} \text{ cm}^{-1}$. Splitting in the $g_{\perp}$ region is unobserved due to line-width and it is estimated that $|A_{\perp}| \sim 1 \times 10^{-4} \text{ cm}^{-1}$. Interestingly the hyperfine splitting constants for $^{101}\text{Ru}(\text{H}_2\text{O})_6^{3+}$ are reduced by at least a factor of two compared to those of $^{101}\text{Ru}(\text{NH}_3)_6^{3+}$. One reason for this is believed to be the $\pi\pi$ - $d\pi$ interaction (Bottcher *et al.* 1979) between oxygen lone pairs and metal t_2 orbitals. The spin-density thus gets localised onto the aquo ligand. This cannot happen in the case of the amine complex. The results of processing the g values are in table 3. Two possible solutions differing in the signs of g_z exist. Solution 1 has larger K but smaller Δ/λ , $\Delta E_1/\lambda$ and $\Delta E_2/\lambda$. Using $\lambda \sim 1000 \text{ cm}^{-1}$, the Δ values of solutions 1 and 2 are ~ 350 and $\sim 2500 \text{ cm}^{-1}$ respectively. Since experimental information on ΔE_1 and ΔE_2 is lacking, only a tentative choice can be made between the two solutions. Bernhard *et al.* (1984) has reported only the first solution with no explicit mention of the second solution and their crystal field parameter is negative (-350 cm^{-1}) apparently due to a different sign convention. Since the trigonal distortion of the $\text{M}(\text{H}_2\text{O})_6^{3+}$ ions in β -alums is of a minor nature in a crystallographic sense the first solution with $\Delta \sim 350 \text{ cm}^{-1}$ is probably appropriate. The sign of Δ is positive meaning that the A state lies below the E state. The $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ ion doped in β -alum is a model example of weak trigonal distortion. The K value of solution 1 affords $k = 1.15/1.24 = 0.93$.

2 Tris(2,2'-bipyridine)ruthenium(III) cation, $\text{Ru}(\text{bpy})_3^{3+}$.

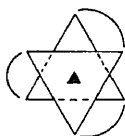
The bpy complexes of ruthenium are of considerable current interest in relation to photochemical sensitisation and catalysis. The electronic structure of $\text{Ru}(\text{bpy})_3^{3+}$ (2) is of relevance in this context. The powder ESR spectrum of this complex (PF_6^- salt in a diamagnetic host lattice) was reported and analysed by DeSimone and Drago (1970). Confusion regarding the signs of parameters had prompted a reanalysis (Kober and Meyer 1983).



(1)



(2)



The $\text{Ru}(\text{bpy})_3^{3+}$ ion had D_3 symmetry and provides a good example of trigonal distortion brought about by tris chelation of a symmetrical bidentate ligand. The observed ESR spectrum is axial (table 3) and it is presumed that $g_z (= g_{||})$ coincides with the C_3 axis. The g values permit two solutions for the parameters (table 3). By a systematic comparison of the ESR spectra of $\text{Fe}(\text{bpy})_3^{3+}$, $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Os}(\text{bpy})_3^{3+}$ Kober *et al.* (1983) concluded that solution 1 is correct. The similarity in the ESR characteristics of the ions $\text{Ru}(\text{H}_2\text{O})_6^{3+}$ and $\text{Ru}(\text{bpy})_3^{3+}$ is noteworthy.

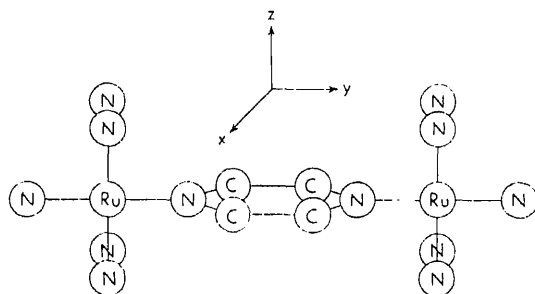
Table 3. The g -values and derived parameters.

Compound	Solution No.	g_x	g_y	g_z	a	b	c	K	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	(1)	-2.514	-2.514	-1.489	0.743	0.668	0.000	1.152	0.348	0.000	1.422	1.635
	(2)	-2.514	-2.514	1.489	0.298	0.954	0.000	0.858	2.535	0.000	2.478	3.256
$[\text{Ru}(\text{bpy})_3]^{3+}$	(1)	-2.640	-2.640	-1.140	0.705	0.708	0.000	1.156	0.507	0.000	1.414	1.710
	(2)	-2.640	-2.640	1.140	0.382	0.923	0.000	0.932	1.912	0.000	1.999	2.705
$[(\text{NH}_3)_5\text{Ru}(\text{pz})\text{Ru}(\text{NH}_3)_5]^{5+}$	(1)	-2.799	-2.487	-1.346	0.723	0.690	0.030	1.198	0.436	-0.138	1.409	1.687
	(2)	-2.799	-2.487	1.346	0.330	0.943	0.040	0.981	2.314	-0.734	2.171	3.201
$\text{RuCl}_2(\text{HL})(\text{L})$	(1)	-2.470	-2.470	-1.849	0.774	0.632	0.000	1.2057	0.210	0.000	1.444	1.577
	(2)	-2.470	-2.470	1.849	0.153	0.988	0.000	1.2055	4.943	0.000	4.663	5.553

the metal d orbitals of t_2 types span $a_1 + e$ and energetically these are intermediate between the π and π^* orbitals. Thus the $e(d)$ orbital is stabilized by interaction with π^* but destabilized by interaction with $e(\pi)$. The $a_1(d)$ orbital is destabilized by interaction with $a_1(\pi)$ but there is no stabilising mixing. Consequently $a_1(d)$ lies higher than $e(d)$. The five-electron ground state is thus $e(d)^4 a_1(d)^1$ which has A_1 symmetry.

The Creutz-Taube complex

of fundamental importance in relation to our understanding of valence delocalisation, intervalence excitation and related phenomena is the model mixed-valence complex (μ-pyrazine) decamminediruthenium(II, III), $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$, called the Creutz-Taube complex (Creutz 1983). The electronic structure



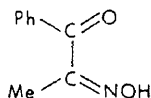
(3)

of the complex has been probed by different workers using the ESR tool (Hush *et al* 1980; Bunker *et al* 1978). Very recently a detailed single crystal work on $[(NH_3)_5Ru(pz)Ru(NH_3)_5]Cl_5 \cdot 5H_2O$ at 3 K has appeared (Stebler *et al* 1984) and we consider this below. Here we have a case of tetragonal-cum-rhombic distortion. Crystal structure work has shown that the two ruthenium atoms in the above complex are structurally equivalent. The angle between the pyrazine plane and the *cis*-NH₃-Ru bonds is 45°. The symmetry of the complex (ignoring protons) is C_{2h} . The overall ESR spectrum is rhombic and the following correspondence is established from angular dependence of g values measured with magnetic field along the crystallographic c -axis or the ab plane: $|g_x| = 2.799$, $|g_y| = 2.487$ and $|g_z| = 1.346$. The molecular axes system shown in (3) is as follows: x , in the plane of the pyrazine ring but perpendicular to the Ru-NH₃-Ru axis; y , the trans-NH₃-Ru-N(pz) axis and z , perpendicular to the pyrazine ring. This axes system chosen to afford $|g_x| > |g_y| > |g_z|$ is different from that of Stebler *et al* (1984). The two possible solutions are in table 3. Both have positive Δ corresponding to the ground state. Stebler *et al* (1984) considered only solution 2. They assign a broad band at about 2000 cm^{-1} in the infrared as the lower (ΔE_1) of the two transitions along the Kramers doublets. In solution 1 the transition energies are less but the margin is not wide enough to ignore this solution. This ambiguity remains. In the axis system chosen, the tetragonal distortion occurs along the x axis and the unpaired electron is localised in an orbital of y^2 symmetry which is parallel to the π^* orbital of the pyrazine ring. The two sets of orbitals can interact and lead to delocalisation of the unpaired electron among the ligand and the metal atoms. The

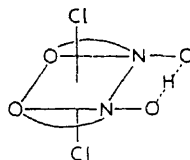
quantitative measure of the extent of delocalisation can therefore be offered from the ESR data.

4.4 *Trans-Ru(HL) (L)Cl₂*

The isonitroketones afford an interesting class of hydrogen-bonded ruthenium(III) species having the *trans*-RuX₂ (X = Cl⁻, Br⁻) moiety (Chakravarty and Chakravorty 1982). A particular example is (5) abbreviated as Ru(HL)(L)Cl₂. The effective ESR symmetry of polycrystalline (5) is axial (table 3). The two possible solutions in this case



(4)



(5)

have nearly equal K values but widely different Δ/λ , $\Delta E_1/\lambda$ and $\Delta E_2/\lambda$. The complex displays a weak transition near 5000 cm^{-1} assignable to ΔE_1 and/or ΔE_2 (Bhattacharya and Chakravorty 1984). This means that solution (2) is correct.

The positive sign and relatively large value of Δ is easy to understand. We identify the Cl-Ru-Cl line as the axis of tetragonal distortion. Since Cl is below N and O in the spectrochemical series, the t_2 level will naturally split placing **b** above **e**. The **e** orbital (d_{xz} , d_{yz}) can be further stabilized by interaction with π^* orbitals of the (HL) (L) moiety but this stabilisation is unavailable for the d_{xy} orbital. We thus have a relatively large separation between **b** and **e**.

5. Concluding remarks

The purpose of this article has been to illustrate the use of ESR data in the hands of chemists for elucidating the electronic structure of some interesting ruthenium(III) compounds (the choice here is entirely subjective). Distorsion from idealised octahedral geometry is more or less the observed rule—be the distortion due to crystal packing forces, ligand asymmetry or electronic factors. Magnetic distortion is not necessarily an expression of geometric distortion. Thus in the Creutz-Taube complex the geometric distortion is along the H₃N-Ru-N(pz) axis, yet the pseudo-tetragonal magnetic axis lies elsewhere. The nature and extent of axial and rhombic distortions can be assessed from the experimental g values in terms of a simple theory. The ambiguity associated with two possible solutions can be resolved in most cases in one way or another. The result can then be translated in terms of orbitals and bonding.

Acknowledgement

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Electron spin resonance of transition metal ions in glasses†

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Abstract. Electron spin resonance (ESR) studies of transition metal ions in glasses have been briefly reviewed. The known relations of spin Hamiltonian parameters to structural geometries around the transition metal ion probes in glasses are summarized. Recent ESR studies in glasses based on the use of Ti^{3+} , VO^{2+} , Mo^{5+} , Cr^{3+} , Fe^{3+} , Mn^{2+} and Cu^{2+} have been emphasized. Merits of ESR in the context of structural elucidation have also been discussed.

Keywords. Electron spin resonance; transition metal ion probes; glass structure.

1. Introduction

It was thirty years ago that the first electron spin resonance (ESR) study of Cu^{2+} in soda-lime silica glasses was reported by Sands (1955). A number of important advances have been made since then and ESR has come to be used as a structural tool in the study of glasses. ESR of glasses is more complex than of crystalline powders because in addition to a distribution of 'crystallite' orientations there is an inherent distribution of crystal fields around the paramagnetic species in a glass. Such a distribution of crystal fields introduces additional breadth to the resonance absorptions due to a distribution in the values of magnetogyric ratio g . A resonance absorption in glass is observed only if g is both isotropic and its value is somewhat insensitive to variations in the degree of distortions of local environments. A wealth of experimental data and their theoretical interpretation now available in literature suggest that g values satisfying the above conditions are quite possible in glasses. Application of ESR to the investigation of glass is essentially based on this finding.

A number of excellent reviews have been written on the subject of ESR in glasses. We particularly refer to those of Wong and Angell (1976) and Griscom (1980) which deal with all aspects of ESR in glasses in sufficient detail. The initial work on ESR of glasses was directed at investigating the magnetic behaviour of various ions in glassy matrices. In recent years studies have been directed more and more towards understanding the structure and nature of bonding in glasses. We feel that ESR of transition metal (TM) ions in glasses has been more promising in this direction. In this short review a modest effort has been made to present a summary of the recent trends in ESR of TM ions in glasses.

2. General principles

The degeneracy of energy states associated with unpaired electron spin is lifted by the application of magnetic field (Orton 1968; Abragam and Bleaney 1970). In general a spin

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of value S ($S = \sum s_i$), has a degeneracy of $(2S + 1)$ and the Zeeman field splits the manifold into $(2S + 1)$ different levels. Transitions can then occur between these states by resonance absorption of energy when electromagnetic radiation of appropriate frequency is impressed upon the system. These transitions are governed by the selection rule, $\Delta m = \pm 1$, where m is the spin magnetic quantum number designating the allowed components of the spin orientation in the magnetic field. In general for an applied magnetic field of about 3000 G, transitions would occur in electron spin system for energy values in the region of a few thousand megahertz frequency. For the case of a single unpaired electron whose angular momentum is only due to the spin the Zeeman interaction gives rise to two spin states, $m = -1/2$ and $m = +1/2$, between which the transition occurs. The energy equation for such a transition is given by

$$h\nu = g_0 \beta H, \quad (1)$$

when H is the applied magnetic field, ν is the microwave frequency, β is the Böhr magneton and g_0 is the magnetogyric ratio for the spin-only case and its value is equal to 2.00234.

In general the situation is more complex. Since the electrons possess angular momentum owing to their orbital motion in addition to their spin angular momentum it often results in spin-orbit coupling. In such situation J ($J = L + S$) will be the relevant good quantum number and the Zeeman field splits the J manifold into various J states. Transitions are now governed by the selection rule $\Delta J = \pm 1$ and g_0 in equation (1) may be replaced by g_L

$$g_L = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}. \quad (2)$$

In rare earth ions where orbital angular momentum of inner d or f electron is not quenched (see later) by crystal fields due to the screening by outer electrons, equation (2) for g_L is found valid. Rare-earth ions generally conform to low-field description (Orton 1968). On the other hand crystal fields arising from neighbouring ions strongly perturb the orbital degeneracy of d electrons of TM ions as a result of which the orbital angular momentum is nearly quenched. The final spin states are therefore influenced to a far greater extent by crystal field than by the spin-orbit interaction. The situation arises in the so-called medium and strong crystal fields as in the case of TM ions in glasses.

The effect of the crystal field and the resulting ground state is shown in figure 1 schematically for the case of a d^1 ion (Ti^{3+} ion) placed in an octahedral coordination (Wong and Angell 1976). The d levels are first split into a triplet (t_{2g}) and a doublet (e_g). The electron occupies the orbital triplet which is at a lower energy. But the degeneracy of this triplet is further lifted by the well-known Jahn-Teller effect through a tetragonal distortion into a b_2 singlet ground state and a doublet e state (the upper doublet is also split into two singlet states, a_1 and b_1). The electron which now occupies the b_2 ground state has an effective orbital angular momentum, L' equal to zero. The situation for d^9 ion is exactly the same except that the ground state is a_1 instead of b_2 . In case of d^3 ions the cubic splitting itself is enough to give a ground state whose L' is zero. For d^5 ions however the free ion ground state itself is an orbital singlet ($L' = 0$). On the other hand the TM ion with even number of electrons (like d^2 , d^4 , d^6 and d^8) generally do not give

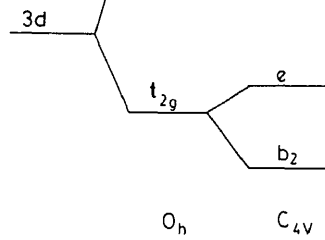


Figure 1. Energy level diagram for d^1 ion in octahedral and tetragonal crystal fields.

characterized by exceedingly short relaxation times and hence broad absorptions even at low temperatures. Usually these ions are of no interest in the ESR study of glasses.

However, we observe ESR resonance for d^1 and d^9 ions at g values slightly different from g_0 . This is due to the spin-orbit coupling (Orton 1968). It arises from a small admixture of the ground state and the excited states with the same J values. In the Zeeman field such a spin-orbit coupling is represented by $\lambda \mathbf{L} \cdot \mathbf{S}$ (where λ is the spin-orbit coupling constant) and it gives rise to resonance at two principal g values (Pryce 1950):

$$g_{\parallel} = g_0 \left[1 - \frac{4\lambda}{\Delta E_{b_2 \rightarrow b_1}} \right], \quad (3)$$

$$g_{\perp} = g_0 \left[1 - \frac{2\lambda}{\Delta E_{b_2 \rightarrow e}} \right], \quad (4)$$

where $\Delta E_{b_2 \rightarrow b_1}$ and $\Delta E_{b_2 \rightarrow e}$ represents the energy difference between the levels b_2 and b_1 and b_2 and e respectively.

In the case of d^3 and d^5 ions the spin-orbit coupling helps to lift the spin degeneracy of orbital-singlet ground state into two and three Kramers doublets respectively. Transitions between some of these levels give rise to resonances at g values very much different from g_0 . This case is dealt with more clearly later in the formalism of spin Hamiltonian.

Further, the nucleus of the paramagnetic species may possess a nuclear spin I greater than zero which interacts with the electron spin giving rise to the well-known hyperfine splitting of resonance lines. Each resonance is split into $(2I + 1)$ lines in such cases. The nuclear spin of neighbouring atoms can also couple with the spin-angular momentum of the unpaired electron which results in the so-called superhyperfine splitting. If the total spin of the neighbouring ions is I' the resonance is further split into $(2I' + 1)$ lines.

All these situations may be analysed by employing a spin Hamiltonian in the framework of perturbative quantum mechanics. A general spin Hamiltonian (Griscom 1980) which takes care of all terms adequately is given as

$$\mathcal{H} = \beta \tilde{H} \cdot \tilde{g} \cdot \tilde{S} + \tilde{I} \cdot \tilde{A} \cdot \tilde{S} + \tilde{S} \cdot \tilde{D} \cdot \tilde{S} \quad (5)$$

The first term on the right side of (5) corresponds to the Zeeman term, the second term

indicates the hyperfine interactions and the third term expresses the total effect of the crystal field. A is known as the hyperfine splitting constant and D is a crystal field parameter. g , A and D are tensor quantities. In an actual calculation of the eigenvalues of the Hamiltonian by perturbation method a knowledge of the hierarchy of the magnitude of these terms is required. Since the term corresponding to hyperfine splitting is least in energy, it is the last term in the perturbation treatment. The explicit form of spin Hamiltonian appropriate for particular ions in various situations is given in later sections. The details of perturbative treatment of the Hamiltonian is also given for some cases.

In an actual experiment the frequency of the microwave energy is kept constant and the magnetic field is varied. The spectrum corresponds to a derivative of the microwave absorption as a function of magnetic field. The spectrum contains information about various ESR or spin Hamiltonian parameters. The knowledge of these parameters gives insights into the structure and bonding aspects of glasses. A complete knowledge of spin Hamiltonian parameters is obtained from simulating the spectral features by varying these parameters and fitting the simulated spectrum to the experimental one. The computer simulation of ESR spectra of TM ions in glasses has been reported by various workers (Taylor and Bray 1970; Kliava and Purans 1980; Bals and Kliava 1983).

In an ESR experiment variation of the microwave absorption is studied as a function of magnetic field. Most of the ESR studies reported for TM ions in glasses have been performed in the X -band (~ 9 GHz) frequency, except for a few low frequency measurements. In places where low frequency (S -band) measurements are quoted, we state that specifically.

3.1 d^1 ions (Ti^{3+} , VO^{2+} and Mo^{5+})

The ESR spectrum of d^1 ions in glasses can be described by the following axially symmetric spin Hamiltonian:

$$H = g_{\parallel} H_z S'_z + g_{\perp} (H_x S'_x + H_y S'_y) + A_{\parallel} I_z S'_z + A_{\perp} (I_x S'_x + I_y S'_y), \quad (6)$$

where the parallel and perpendicular signs indicate the corresponding components of the parameters. $S' = 1/2$ and $I = 0$ for ^{48}Ti and $7/2$ for ^{57}V . g values are given by (3) and (4). The derivation of these equations is based on pure electric field effects of the surrounding ions and the spin-orbit coupling effects. The covalency effects had not been considered. If the covalency effects are also included, Kivelson and Lee (1964) have shown that (3) and (4) become

$$g_{\parallel} = g_0 \left[1 - \frac{4\alpha^2 \beta^2 \lambda}{E_{b_2 \rightarrow b_1}} \right], \quad (7)$$

$$g_{\perp} = g_0 \left[1 - \frac{\delta^2 \beta^2 \lambda}{E_{b_2 \rightarrow e}} \right], \quad (8)$$

$$A_{\parallel} = -P \left[\beta^2 \left(\frac{4}{7} + \kappa \right) + \Delta g_{\parallel} + \frac{3}{4} \Delta g_{\perp} \right], \quad (9)$$

$$A_{\perp} = P \left[\beta^2 \left(\frac{2}{7} - \kappa \right) + \frac{1}{4} \Delta g_{\perp} \right], \quad (10)$$

1a Ti^{3+} : Yafaev and Yoblov (1962) and Garif'yanov and Tokareva (1964) were the first to study ESR of Ti^{3+} in alkali silicate and phosphate glasses. They observed resonances with g varying from 1.92–1.94. These spectra are characterized by short spin-lattice relaxation times and large negative g shifts ($g < g_0$) attributable to small trigonal field splitting of low lying orbital triplet resulting from the predominantly octahedral field. This is the reason why ESR of Ti^{3+} in many systems is not observable at room temperature. Peterson and Kurkjian (1972) studied the low frequency (0.5 GHz) ESR of calcium borate glasses containing ^{47}Ti ($I = 5/2$) and ^{49}Ti ($I = 7/2$) which substituted for the natural ^{48}Ti ($I = 0$) and conclusively assigned the resonance to Ti^{3+} . They could observe hyperfine splitting in 0.5 GHz measurements (S-band) which they showed is due to the fact that linewidths at low frequencies become narrower (figure 2). Kurkjian and Peterson (1974) later applied ESR of Ti^{3+} to the study of Ti^{3+} – Ti^{4+} equilibrium in TiO_2 – SiO_2 glasses at low frequencies (S-band). They found that Ti^{3+} concentration increases with the partial pressure of hydrogen and temperature. The kinetics of oxidation and reduction has been found to be governed by the rapid outward and inward diffusion of hydrogen molecules. These authors have also pointed out that Ti^{4+} ions in six-fold coordination only are reduced by hydrogen which results in six coordinated Ti^{3+} ions in the melt. Ti^{4+} ions most of which are present in 4-fold coordination are difficult to reduce, Iwamoto *et al* (1983b) have studied Ti^{3+} – Ti^{4+} reaction in reduced sodium silicate glasses and found that Ti^{3+} ions are coordinated preferentially to nonbridged oxygens. They also suggest that $[Ti^{3+}O_4O_2^-]$ and $[Ti^{3+}O_3O_3^-]$ complex ions are most probable in the reduced sodium silicate glasses.

1b VO^{2+} : Several ESR investigations of ESR glasses reported in literature are based on the use of V^{4+} ion. ESR spectrum of V^{4+} is rich in hyperfine structure due to the ^{51}V nucleus ($I = 7/2$) and can be easily observed at room temperature. A typical spectrum is given in figure 3. The axially symmetric spin Hamiltonian given in (6) which is appropriate for V^{4+} ions was analysed first by Hochstrasser (1966) and Hecht and Johnson (1967). They independently reached the conclusion that V^{4+} ion in glasses is present as vanadyl, VO^{2+} ion. Many researchers (Toyuki and Akagi 1972; Bogomolova

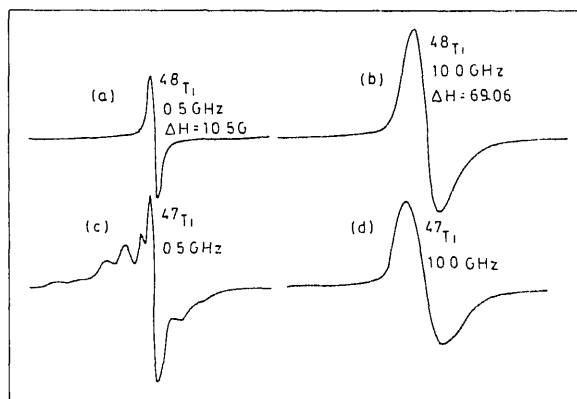


Figure 2. ESR spectra of $30CaO \cdot 69B_2O_3 \cdot 1TiO_2$ glass. (a) and (c) were obtained at 0.5 GHz

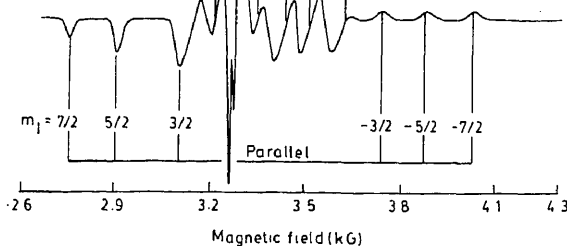


Figure 3. A typical ESR spectrum of VO^{2+} in a vanadium glass. Both parallel and perpendicular components of hyperfine structure are well resolved (after Bandyopadhyay 1981).

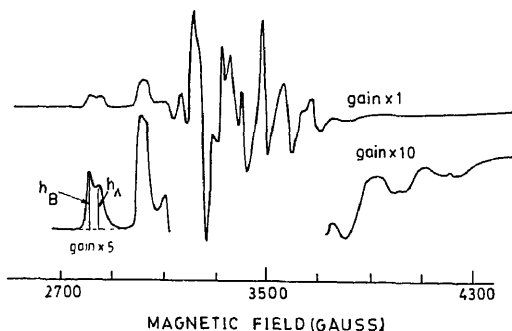


Figure 4. Representative ESR spectrum of VO^{2+} in $63\text{BeO}-37\text{P}_2\text{O}_5$ glass showing two sets of hyperfine structure (after Hosono *et al* 1980).

et al 1974; Paul and Assabghy 1975; Momo *et al* 1981b; Bandyopadhyay 1981; Seth *et al* 1983; Bogomolova *et al* 1983b) employed ESR of VO^{2+} to study the structure of glasses. Recently structural anomaly of phosphate glasses has been investigated in great detail. Bogomolova *et al* (1978a) studied $\text{RO}-\text{B}_2\text{O}_3$ glasses ($\text{R} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{Zn}$) and found two sets of hyperfine structure (HFS-A and HFS-B) in $\text{MgO}-\text{P}_2\text{O}_5$ and $\text{ZnO}-\text{P}_2\text{O}_5$ systems and one set of hyperfine structure (HFS-A) for other systems. They concluded that the coexistence of two kinds of local structures is the origin of the anomalous ESR spectra of $\text{MgO}-\text{P}_2\text{O}_5$ and $\text{ZnO}-\text{P}_2\text{O}_5$ glasses (Kordes *et al* 1953). Hosono *et al* (1980) made a detailed analysis of the ESR of VO^{2+} in $\text{RO}-\text{P}_2\text{O}_5$ and $\text{R}'_2\text{O}-\text{P}_2\text{O}_5$ glasses ($\text{R} = \text{Bi}, \text{Mg}, \text{Sr}, \text{Ba}, \text{Ca}, \text{Ni}, \text{Pb}, \text{Zn}, \text{Cd}$ and $\text{R}' = \text{Li}, \text{Na}, \text{Cs}, \text{Ag}$). A spectrum showing two sets of hfs is shown in figure 4. They found a correlation between the ionic potential (Z/R) of network modifiers and the appearance of two hyperfine structures. Their results are summarized in figure 5. Though it was shown that the super-position of two hyperfine structures was observed only for systems with network modifiers whose $Z/\text{R} \geq 2$, this study has not satisfactorily explained the anomaly.

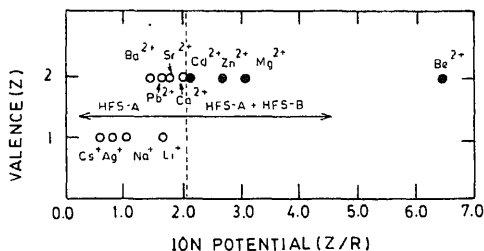


Figure 5. Correlation between the ionic potential of the network modifier and the appearance of the two sets of hyperfine structure, HFS-A and HFS-B in the ESR of VO^{2+} incorporated into metaphosphate glasses (after Hosono *et al* 1980).

gomolova *et al* (1983b) in another study of VO^{2+} in binary $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ and $\text{SiO}_2\text{-P}_2\text{O}_5$ glasses and ternary $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ glasses have shown that the behaviour of ESR spectra is even more complex. Though they found two kinds of hyperfine structure for aluminophosphate glasses ($Z/R \approx 5/2$ for Al^{3+}) in accordance with Hosono's correlation, only HFS-B has been observed for silicophosphate glasses ($Z/R \approx 10$ for Si^{4+}). However these authors have found an excellent agreement of the ESR parameters of V^{4+} ions in crystalline AlPO_4 and SiP_2O_7 powders with those of HFS-B spectrum from aluminophosphate, aluminosilicophosphate and aluminoborophosphate glasses. It has been suggested that the electronic structure of paramagnetic species responsible for HFS-B spectrum in glasses acts as modifiers and is situated in relatively small holes of three-dimensional phosphate networks.

In another interesting application of ESR of VO^{2+} , Sunandana and Bhatnagar (1984) studied hopping conduction in $\text{V}_2\text{O}_5\text{-MO}_2$ glasses ($M = \text{Ge, Se, Te}$). They have examined the spectra in the temperature range 298–498 K and observed dramatic and reversible temperature dependences by way of progressive broadening and eventual appearance of the hyperfine structure. This behaviour has been attributed to a thermally activated delocalization of the $3d^1$ electron spin leading to hopping electronic conduction. They have also found that covalency of the V-O bond increases from GeO_2 to TeO_2 to SeO_2 .

Mo^{5+} : Garif'yanov and Fedotov (1963) were the first to report ESR of Mo^{5+} ions in borate and phosphate glasses. They studied temperature and frequency dependence of the Mo^{5+} spectra. A typical spectrum is given in figure 6. Baugher and Burke (1972) studied ESR of Mo^{5+} in phosphate glasses and analysed the spectra using spin Hamiltonian given in (6). They found that coordination of Mo^{5+} ion is highly distorted from octahedral symmetry. They suggested that Mo^{5+} is present as a molybdenyl ion, MoO^{3+} in phosphate glasses. However, in a recent study of $\text{B}_2\text{O}_3\text{-SiO}_2\text{-O-MoO}_3$ glasses, Simon and Nicula (1983) suggest three different site symmetries (cubic, axial and rhombic) for Mo^{5+} from their analysis of resonance lineshapes. They have also investigated the effect of composition, MoO_3 concentration and preparation temperature on the ESR spectra. Increasing Na_2O content has the effect of altering the four coordinated borons which in turn affect the concentration of Mo^{5+} ions in various symmetries. The effect of holding time of the melt on the equilibrium concentration of Mo^{5+} ions has been studied by Simon and Nicula (1983). They have also found that the concentration of Mo^{5+} ions increases with increasing Na_2O content.

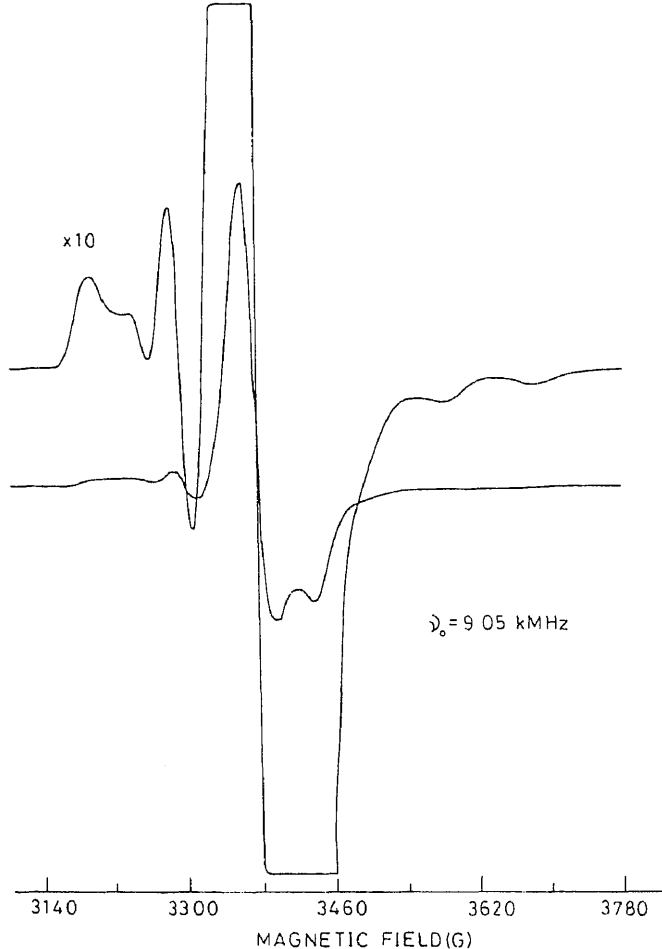


Figure 6. A typical ESR spectrum of Mo^{5+} in a potassium phosphomolybdate glass (after Selvaraj and Rao 1985).

Sperlich (1973) studied the hyperfine structure of $\text{MoO}_3\text{-TeO}_2$ and $\text{MoO}_3\text{-P}_2\text{O}_5$ glasses enriched with ^{95}Mo isotope. They found that d -electron is mainly localized on one molybdenum site. The transfer rate of the d -electron (hopping frequency) is lower than the hyperfine splitting in frequency units even at room temperature. ESR of Mo^{5+} has also been used to estimate $\text{Mo}^{5+}/\text{Mo}_{\text{total}}$ in MoO_3 -containing glasses (Patel and Bridge 1983; Selvaraj and Rao 1985).

There have been few reports on the ESR of Cr^{5+} ions. These results are discussed along with the spectra of Cr^{3+} . However, no significant ESR spectra of W^{5+} ions (see Wong and Angell 1976 for earlier reports) have appeared in recent times.

3.2 d^3 (Cr^{3+}) and d^5 (Fe^{3+} and Mn^{2+}) ions

We noted earlier that the degeneracy of odd electron TM ions is partially lifted by the

in the Zeeman-split Kramers doublet. The spin Hamiltonian (Bleaney and Stevens 1953) employed for these ions is given below:

$$\mathcal{H} = g_0 \beta H + D[S_z^2 + \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2), \quad (11)$$

where D and E are the crystal field parameters representing axial and rhombic distortions respectively. It may be seen that the crystal field effects enter as second order terms in spin quantum number. Castner *et al* (1960) were the first to apply the above spin Hamiltonian successfully to explain the ESR spectra of Fe^{3+} (d^5) ions in glasses. In this classic work they assumed the primacy of the crystal field terms and treated Zeeman term as a perturbation. It is clear from the Hamiltonian in (11) that by dropping all terms other than DS_z^2 , i.e., by switching on the axial crystal field, the degeneracy is lifted giving rise to $\pm m$; $\pm(m-1) \dots \pm \frac{1}{2}$ states for the odd electron TM ions. This accounts for the resulting Kramers doublets. The two crystal field parameters D and E can be combined into a single parameter by taking the ratio $E/D = \lambda$ (not to be confused with the spin-orbit coupling constant). The spin Hamiltonian can then be analysed with the limiting values of λ . It has been shown (Wickman *et al* 1965) that $\lambda = 0$ to $\frac{1}{2}$ covers practically all significant crystal field situations arising in solids from fully axial ($\lambda = 0$) to fully rhombic ($\lambda = \frac{1}{2}$) symmetry. For these extreme values of λ , g values for which resonances occur for d^3 and d^5 ions are summarized below:

	$\lambda = 0$	$\lambda = \frac{1}{2}$
d^3	$g_{\parallel} = 2$ $g_{\perp} = 5$	—
d^5	$g_{\parallel} = 2$ $g_{\perp} = 6$	$g_{\text{eff}} = 4.3$

It is significant that in the case of d^5 ions $g_{\text{eff}} = 4.3$ resonance observed for rhombic symmetry has been found to be remarkably isotropic. The actual variation of the individual g_x , g_y and g_z for d^5 ions as a function of λ (Wickman *et al* 1965) is shown in Figure 7.

(a) Cr^{3+} : Though the ESR of Cr^{3+} , a d^3 ion, has not been widely studied in glasses, a few interesting studies have been reported recently. A typical spectrum is given in Figure 8. The spin Hamiltonian given in (11) was first analysed for Cr^{3+} by Garif'yanov and Zaripov (1964) and later more exactly by Zakharov and Yudin (1965). The latter authors had shown that the transitions in the two Kramers doublets yield two resonances at $g_{\perp} = 5.0$ and $g_{\parallel} = 1.77$ in agreement with their experimental results. Recently Fuxi *et al* (1982) have pointed out that the transitions can occur not only within the Kramers doublets but also between the levels in different Kramers doublets. Landry *et al* (1967) noted that as the concentration of chromium increases, the resonance at $g \simeq 2.0$ becomes more dominant. This feature was attributed to exchange-coupled Cr^{3+} ion pairs. The low field feature (at $g \simeq 5.0$), which reduces in intensity as the concentration of chromium increases, was attributed to isolated, octahedrally coordinated Cr^{3+} ions. Recently Ardelean *et al* (1984) have investigated the concentra-

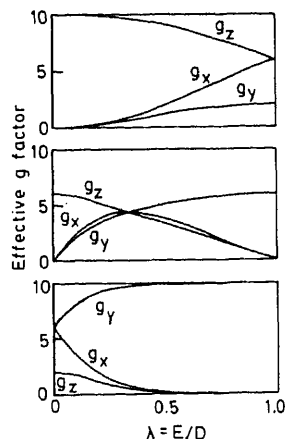


Figure 7. The effective g values for the spin Hamiltonian given in equation (11) plotted against $\lambda = E/D$ (after Wickman *et al* 1965).

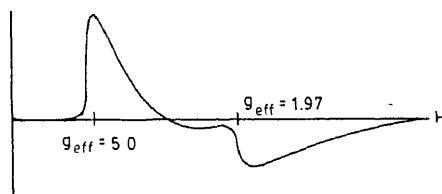


Figure 8. ESR spectrum of Cr^{3+} in alumino-zinc phosphate glass containing 0.57 wt % Cr_2O_3 (after Landry *et al* 1967).

tion dependence of spectrum in $x\text{Cr}_2\text{O}_3 \cdot (1-x)[3\text{B}_2\text{O}_3\text{-PbO}]$ glass and found a similar behaviour. However they found evidence for the presence of both Cr^{3+} and Cr^{5+} in glasses. Cr^{5+} ions which are in small proportion produce resonance at $g = 1.98$. This resonance is superimposed upon another resonance at $g = 1.97$ due to exchange coupled Cr^{3+} ion pairs. Earlier, Iwamoto and Makino (1980) investigated the state of chromium ions in soda-silicate glasses under various oxygen pressures. In glasses produced in air or under moderately reducing conditions, three ESR absorptions were observed near $g = 2.0$ (sharp), $g = 2.0$ (broad) and $g = 5.0$. These three absorptions were assigned to isolated Cr^{5+} ions, strongly coupled Cr^{3+} ion pairs and isolated Cr^{3+} ions in orthorhombic crystal field respectively. An absorption attributable to weakly coupled Cr^{3+} ion pairs was observed near $g = 2.3$ in glasses produced in reducing atmosphere.

In an interesting application of ESR of Cr^{3+} ions Zhilinskaya *et al* (1983) investigated the effect of pressure treatment, temperature and annealing on the structure of chalcogenide glasses. They found that the ESR parameters of Cr^{3+} impurity ions in As_2Se_3 glass and $5\text{Cu}95\text{As}_2\text{Se}_3$ glass varied considerably by the application of pressure. The variations have been attributed to pressure induced structural changes

ly discussed. In another interesting study Bruckner *et al* (1980) have employed the ESR spectrum of Cr^{3+} to investigate structural anisotropies in silicate glass fibres. They have found that the short-range order of Cr^{3+} ion is identical in nature both in bulk and fibre glasses. The Cr–O bonding in CrO^{3+} is less covalent in the fibre than in the bulk glass. It was also found to be orientation-dependent. In another study of Cr^{3+} in phosphate, metaphosphate and fluoride glasses, Fuxi *et al* (1982) found g values to be highest in phosphate and lowest in fluoride glasses. Such an observation is in agreement with the expectation that the ionicity of Cr–O bond is lowest in phosphate and highest in fluoride glasses.

Fe^{3+} : The ESR spectrum of Fe^{3+} in glasses is characterized by a sharp, well-defined resonance at $g = 4.3$ and relatively weak resonances at $g = 2, 6$ and 10 . A typical ESR spectrum is shown in figure 9. As stated earlier in this section, the features of ESR spectrum of Fe^{3+} in glasses were successfully explained by Castner *et al* (1960) by using the spin Hamiltonian given in (11). These authors associated the $g = 4.3$ resonance with Fe^{3+} in a network-forming (tetrahedral) site. However, it was shown by Loveridge and Keane (1971) that this resonance can be produced by rhombic symmetry of either octahedral or tetrahedral coordination of Fe^{3+} . These authors have described different possible coordination environments associated with resonances at $g = 2, 4.3$ and 6 . The $g = 2.0$ resonance can be caused by both axiality of the crystal field and spin-spin interaction. The spin-spin interaction appears to be the primary cause of $g = 2.0$ resonance in glasses containing higher concentration of Fe^{3+} ions (Kurkjian and Sigety 1978; Moon *et al* 1975). Peterson *et al* (1974) have argued that $g = 4.3$ resonance of Fe^{3+} can also result from a large spread of $g_{\perp}$ (6.0) and $g_{\parallel}$ (2.0) resonances along with a substantial negative correlation. This suggestion is repudiated in the work of Ramo *et al* (1981a) who showed that the $g = 4.3$ resonance is due to Fe^{3+} ions in octahedral sites in their studies of selected silicate glasses.

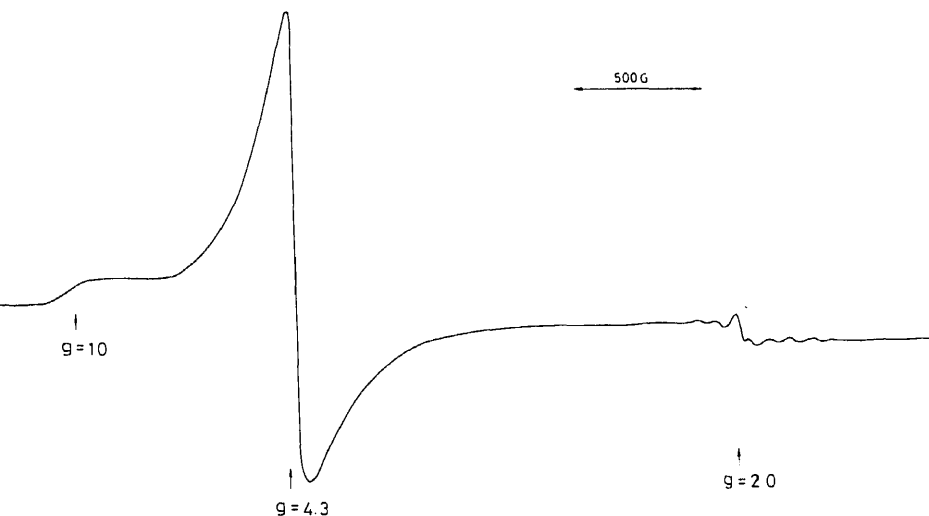


Figure 9. ESR spectrum of Fe^{3+} in PbO-PbF_2 glass (after Rao and Rao 1985).

variation of Na_2O content (Loveridge and Parke 1971). However, Danielson and Schreurs (1980) have found changes in line shape and intensity of $g = 4.3$ resonance with composition in $x\text{MO} \cdot y\text{Al}_2\text{O}_3 \cdot z\text{SiO}_2$ glass containing 0.1 mol% Fe_2O_3 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Mg}$). The effect is most pronounced in Ba and Sr glasses, less so in Ca glass and quite small in Mg glass. They attributed this behaviour to change in coordination from four-fold to six-fold for Fe^{3+} ion without sufficiently corroborative evidence for such an assignment. Iwamoto *et al* (1983a) recently have investigated the state of Fe^{3+} ion and $\text{Fe}^{3+}\text{-F}^-$ interaction in $x\text{CaF}_2 \cdot (1-x)\text{CaO} \cdot \text{SiO}_2$ ($0 \leq x \leq 0.3$) glasses by ESR. Two resonances were observed near $g = 2.0$ and $g = 4.3$ which were assigned to Fe^{3+} ions with dipole-dipole interactions and isolated Fe^{3+} ions in rhombic symmetry, respectively. The relative magnitude of Fe^{3+} centres giving rise to dipole-dipole interaction depended on CaF_2 content and it exhibited a maximum at 10 mol% of CaF_2 . Iwamoto *et al* (1983a) discussed this behaviour in the light of 1 s binding energy of and negative partial charge on fluorine; the latter quantities behave in a similar way with composition. A similar composition dependence of line intensity of $g = 2.0$ resonance has been found in $\text{BaO-B}_2\text{O}_3$ glasses (Kishore *et al* 1984). The intensity of $g = 2.0$ resonances shows a maximum at 40 mol% BaO while the intensity of $g = 4.3$ resonance shows a minimum at the same composition. This anomalous composition dependence of intensities has however not been clearly understood.

We have investigated ESR of Fe^{3+} in lead oxide-lead halide glasses (Rao and Rao 1985). The spectral features are quite drastically affected by composition in PbO-PbCl_2 glasses. In PbCl_2 -rich composition $g = 6.0$ resonance has been observed in addition to $g = 4.3$ resonance. The intensity of $g = 6.0$ resonance increases and the intensity of $g = 4.3$ resonance decreases with increasing PbCl_2 content suggesting that more (axially) symmetric sites are available for Fe^{3+} in PbCl_2 -rich glasses. However, the spectra of PbO-PbF_2 glasses do not show such composition dependence. This difference between the two glass systems can be attributed to the difference in sizes of chloride and fluoride ions as also the tendency of fluorine to enter network positions.

Komatsu and Soga (1980) studied the crystallization process of sodium-iron-silicate glass and found that the $g = 4.3$ resonance disappears and $g = 2.0$ resonance sharpens in the process of crystallization. They attributed this behaviour to the removal of distortions and randomness in the environment of Fe^{3+} ions during crystallization. Baiocchi *et al* (1980) who studied the high temperature ESR of Fe^{3+} in lead silicate glass also observed the disappearance of $g = 4.3$ resonance and narrowing of $g = 2.0$ resonance at high temperature. However, these authors have attributed the narrowing of $g = 2.0$ resonance to diffusion of Fe^{3+} ions in the glass as diffusion causes narrowing due to reduction of dipolar broadening.

The clustering tendency of Fe^{3+} ions in $2\text{OFe}_2\text{O}_3[3\text{B}_2\text{O}_3(1-x)\text{PbO}_x\text{GeO}_2]$ glasses has been reported by Burzo *et al* (1980). At high temperatures of equilibration isolated Fe^{3+} ion sites appear to be favoured. But with increasing GeO_2 in the glass (which increases oxygen concentration) there appears a maximum in $g = 4.3$ resonance as a function of x . This is perhaps due to larger distortion of tetrahedra in intermediate compositions.

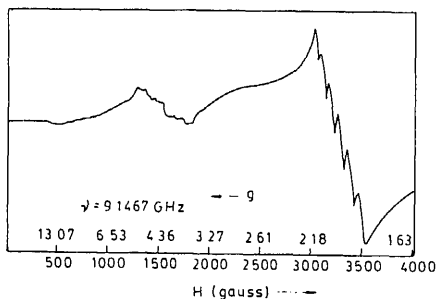


Figure 10. A typical ESR spectrum of Mn^{2+} in a silicate glass (Schreurs 1978).

Mn^{2+} : The ESR spectrum of Mn^{2+} in oxide glasses are characterized by an intense resonance at $g = 2.0$ with hyperfine structure, an absorption at $g = 4.3$ and a distinct shoulder at $g = 3.3$. In chalcogenide glasses the spectra are qualitatively similar to those of oxide glasses though the relative intensity of $g = 4.3$ resonance is greatly enhanced in some systems (Wong and Angell 1976). A typical spectrum of Mn^{2+} in an oxide glass is given in figure 10. Although Mn^{2+} shares the same $3d^5$ ($^6S_{5/2}$) electronic structure as Fe^{3+} , its ESR spectra are generally quite different, firstly due to the addition of hyperfine structure ($I = 5/2$ for ^{55}Mn) and secondly due to generally much smaller crystal field splittings. Spin Hamiltonian which includes hyperfine interaction also is appropriate for this case:

$$\mathcal{H} = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + A.S.I. \quad (12)$$

On the basis of the treatment of the spin Hamiltonian by Castner *et al* (1960) for Fe^{3+} , Tucker (1962) suggested existence of two distinct sites: one with large E value (rhombic case) giving rise to $g = 4.3$ resonance and the other with both D and E very much less than Zeeman energy giving rise to predominant resonance at $g = 2.0$. de Wijn and van Alderen (1967) and Griscom and Griscom (1967) were the first to attempt a detailed explanation of the ESR spectrum of Mn^{2+} in oxide glasses in terms of the spin Hamiltonian parameters. Griscom and Griscom (1967) suggested that the Mn^{2+} sites in alkali borate glasses are characterized by $(E/D) \sim 1/3$ and $(D)/h \sim 2$ GHz. Further they suggested that a broad distribution of sites with different D and E values with a probable constraint of $E/D \sim 1/3$ is present in these glasses. A transition can be observed only if the resonance energy is stationary with respect to variations in D and E . Similar conclusions were drawn by Taylor and Bray (1972) from their study of ESR of Mn^{2+} in strontium borate (crystalline and glassy).

The magnitude of the hyperfine splitting constant A provides a measure of covalency between Mn^{2+} ion and its ligands. Van Wieringen (1955) empirically determined a positive correlation between A and ionicity of the manganese-ligand bond. On this basis it was found that Mn^{2+} is quite ionic in alkali borate and phosphate glasses ($A = 92$ G) and less ionic in silicate glasses ($A = 86-88$ G) (Schreurs 1978; de Wijn and van Alderen 1967). We have investigated ESR spectra of Mn^{2+} in K_2SO_4 - $ZnSO_4$ glasses (Sundar and Rao 1982) and lead oxide-lead halide glasses (Rao and Rao 1985) and found that Mn^{2+} is highly ionic in sulphate glasses ($A = 92$ G) and less ionic in lead

The hyperfine structure at $g = 4.3$ resonance in chalcogenide glasses is well resolved although it is complicated by additional structure. This feature has been employed in the study of structural aspects of chalcogenide glasses (Watanabe *et al* 1976; Kumeda *et al* 1978; Zhilinskaya *et al* 1980; Durney 1980; Kaitai *et al* 1983; Barnier *et al* 1983). The hyperfine splitting constants of Mn^{2+} in chalcogenides are very low ($A = 60\text{--}65\text{G}$) suggesting that Mn^{2+} is very strongly covalently bonded in these glasses. It was also suggested (Watanabe *et al* 1976) that $g = 4.3$ resonance arises from the Mn^{2+} ions incorporated into the network. It is generally believed that Mn^{2+} is four-coordinated in chalcogenide glasses except in $\text{GaS}_{3/2}\text{-GeS}_2\text{-MnS}$ glass (where the value of hyperfine splitting constant is slightly higher $A = 71\text{G}$) in which Mn^{2+} has been shown to be six-coordinated by uv-visible spectroscopy (Barnier *et al* 1983). Kumeda *et al* (1978) investigated the structural changes in chalcogenide glasses by monitoring the hyperfine structure of the resonance at $g = 4.3$ induced by various processes such as annealing, illumination or application of high pressure. These processes cause a change of lineshape of the hyperfine structure and also hyperfine splitting constant both of which reflect the bonding characteristics around manganese. From these studies it has been concluded that the randomness of amorphous structure decreases by annealing and increases by illumination or application of pressure. Additional hyperfine structure at $g = 4.3$ resonance has been the subject of study of many investigations (Lazukin *et al* 1975; Chepeleva *et al* 1977; Schreurs 1978; Zhilinskaya and Lazukin 1982). Lazukin *et al* (1975) interpreted the double hyperfine structure at $g = 4.3$ in chalcogenide glasses as the superposition of two unequal sextets with a shift in the isotropic g factor ($\Delta g \simeq 0.08$). Schreurs (1978) found superposition of these different hyperfine structures with $\Delta g \simeq 0.024$. However, these explanations are not unique. Zhilinskaya and Lazukin (1982) attribute the additional hyperfine structure to the forbidden hyperfine transitions.

In glasses containing PbO such as PbO-SiO_2 , PbO-TeO_2 and PbO-PbCl_2 (Bogomolova *et al* 1978; Ardelean *et al* 1980; Rao and Rao 1985), $g = 4.3$ resonance has been found to be quite intense and a single set of hyperfine structure is well resolved, particularly in PbO -rich compositions. Rao and Rao (1985) propose that Mn^{2+} occupies network positions with a coordination polyhedra of the type, $[\text{MnO}_2\text{Cl}_4]$ in PbO-PbCl_2 glasses. The spectral features (particularly at $g = 2.0$) which are drastically affected by composition, are explained by the structural model for these glasses. It was also found that the spectra of Mn^{2+} in PbO-PbF_2 glasses are quite similar to those of oxide glasses (absence of intense, well-resolved $g = 4.3$ resonance) whereas the spectra for PbO-PbCl_2 glasses are similar to those of chalcogenide glasses. These differences have been attributed to differences in the role of fluorine and chlorine in glasses (as pointed out earlier in the study of Fe^{3+}).

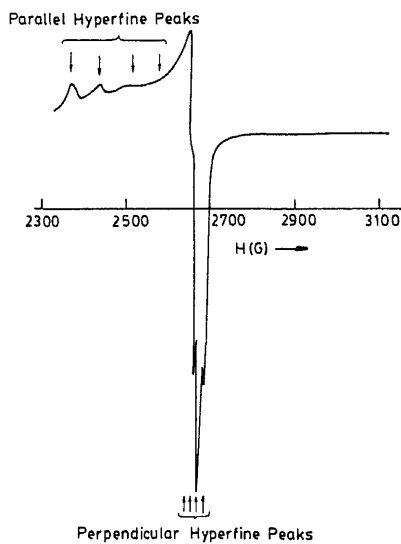
The most important development in this field probably is the application of superposition model analysis of ESR spectra to determine distortions around d^5 ions in glasses. This method was first proposed by Newman (1971) and applied to glasses by Brodbeck and Bukrey (1981) and Kliava (1982). Brodbeck and Bukrey (1981) found from their analysis that a wide range in the magnitude of the crystal field parameters satisfy the condition for the appearance of $g = 4.3$ resonance in Fe^{3+} while the range is much smaller in the case of Mn^{2+} ions. Hence they show that in general the intensity of $g = 4.3$ resonance as compared to that at $g = 2.0$ must be considerably higher for Fe^{3+} .

ions than for Mn^{2+} ions. They have also shown that the resonance at $g = 4.3$ observed in the X -band should be absent in the Q -band as indeed the case. Kliava (1982) employed a gaussian probability density function for variations in D and E in making use of the superposition model. He has shown that D_0/E_0 being equal to 3 and not (D/E) is the rigorous constraint for observing $g = 4.3$ resonance for d^5 ions (D_0 and E_0 are the mean values of D and E respectively). It has also been argued that the distribution functions for the crystal field parameters required for $g = 2.0$ and $g = 4.3$ resonances have negligible overlap. Hence Kliava (1982) supports the earlier conjecture of Tucker (1962) that two dominant resonances observed in Mn^{2+} ESR may be associated with different sites even though it is admitted that demarcation of network former and network-modifier sites is difficult. Nevertheless, it would be possible to assign tentatively such positions in combination with the values of hyperfine splitting constant which are generally lower for tetrahedrally coordinated (network former) Mn^{2+} ions.

3.2d Cu^{2+} : ESR of Cu^{2+} in glasses was studied first by Sands (1955) in soda-lime-silicate glasses and later by Hecht (1968) in soda-boric oxide glasses and Imagawa (1968) in sodium and lithium glasses. A typical ESR spectrum of Cu^{2+} is given in figure 11. The spectra of Cu^{2+} in glasses are characterized by two principal resonances ($g_{\parallel} \approx 2.32$ and $g_{\perp} \approx 2.06$) with four-line hyperfine splitting (due to ^{65}Cu and ^{63}Cu , $I = 3/2$). A spin Hamiltonian given for d^1 ions in (6) can be used for d^9 ion also. Iwagawa's (1968) treatment of the spin Hamiltonian provides the two principal values of g involving covalency parameters and spin-orbit coupling;

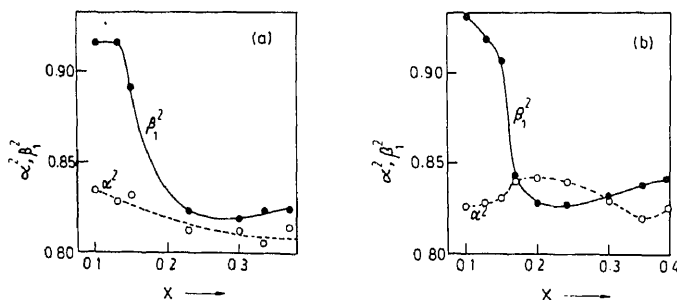
$$g = g_0 \left[1 - \frac{4\alpha^2 \beta_1^2 \lambda}{\Delta} \right], \quad (13)$$

$$g = g_0 \left[1 - \frac{\alpha^2 \lambda}{\Delta} \right], \quad (14)$$



where Δ and λ are the crystal field splitting energy and spin-orbit coupling constant respectively. $(1 - \alpha^2)$ represents the degree of covalency of the (in-plane) σ -bonding while $(1 - \beta_1^2)$ represents the covalency of (out-of plane) π -bonding between Cu^{2+} and the ligands.

The environment of Cu^{2+} in glass is tetragonally distorted octahedron (axially elongated, D_{4h} symmetry). For such distortions $g_{\parallel} > g_{\perp}$. In borate glasses, Cu^{2+} shares oxygens which are part of the boroxyl ring in the network. The lone pair of oxygen can be involved in π -bonding with Cu^{2+} or can be delocalized into boroxyl π -system. Hence there is a competition between boroxyl ring and Cu^{2+} to share the lone pair of oxygen and any changes in the boroxyl network which tilts this balance can be sensed by changes in ESR features. ESR features are quite sensitive to changes in bonding around Cu^{2+} . In his study of sodium and lithium borate glasses, Imagawa (1968) found that α^2 is relatively insensitive to glass composition whereas β_1^2 (or $g_{\parallel}$ and $A_{\parallel}$) is affected by composition (figure 12). The sharp drop in β_1^2 above 15 mol % alkali oxide was taken to reflect a weakening in the average B-O bond strength due to the formation of four-coordinated borons. Since then an increasing number of studies of Cu^{2+} in various borate glasses ($\text{RO-B}_2\text{O}_3$ and $\text{R}'_2\text{O-B}_2\text{O}_3$; $\text{R} = \text{Ba, Sr, Pb, Zn}$ and $\text{R}' = \text{Li, Na, K, Tl}$) have been reported in literature (Bogomolova *et al* 1971; Kawazoe *et al* 1978b; Hosono *et al* 1979; Hosono *et al* 1981; Ohta *et al* 1982; Bogomolova and Jachkin 1983). In all cases, abrupt changes in $g_{\parallel}$ and $A_{\parallel}$ were noted at various concentrations of RO or R_2O for different systems. Similar behaviour was noted for $\text{Na}_2\text{O-P}_2\text{O}_5$ and $\text{K}_2\text{SO}_4\text{-ZnSO}_4$ glasses also (Kawzoe *et al* 1978b). As pointed out earlier sudden changes in $g_{\parallel}$ and $A_{\parallel}$ were attributed to changes in covalency of $\text{Cu}^{2+}\text{-O}$ π -bonding (or weakening of B-O bonding). Kawazoe *et al* (1978a) have estimated basicities of an oxygen in alkali borate glasses by means of MO calculations for molecular models of various borate groups. They have found that the degree of delocalization of the out-of-plane non-bonding level (π -character) decreased in the composition region of 15–20 mol % alkali oxide while in-plane basicity was nearly constant over the composition of 0–35 mol % alkali oxide. However this study does not explain the abruptness of the changes in bonding or ESR parameters. According to present understanding (Bogomolova and Jachkin 1983) of Cu^{2+} spectra of borate glasses, there are three different spectra (I, II and III) with distinct ranges of $g_{\parallel}$ and $A_{\parallel}$ values. For example, spectra I, II and III are obtained for $\text{Na}_2\text{O-B}_2\text{O}_3$ glasses with $5 \leq \text{Na}_2\text{O} \leq 13$, $20 \leq \text{Na}_2\text{O} \leq 37$ and $55 \leq \text{Na}_2\text{O} \leq 75$ respectively. Step-like changes in ESR parameters observed in the region around 17 to 45



different cooling rates. The ESR parameters of this spectrum are much the same as spectrum II, but a significant difference was observed between the thermal stabilities of these spectra. Ardelean *et al* (1984) did not find any significant modification of ESR parameters with increasing copper content in $x\text{CuO} \cdot (1-x) [2\text{B}_2\text{O}_3\text{-Li}_2\text{O}]$ glasses (with $x = 0$ to 30). In sodium borosilicate (Dingkum *et al* 1982) $g_{\parallel}$ changes moderately whereas the other spin Hamiltonian parameters and the covalency of $\text{Cu}^{2+}\text{-O}$ bond remain almost constant. In phosphate glasses (Bogomolova *et al* 1978) also only a linear dependence of ESR parameters was noted with increasing BaO and CaO. Similarly in mixed alkali $\text{Li}_2\text{O-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glasses (Klonkowski *et al* 1983), a monotonic decrease in the values of $g_{\parallel}$ and $A_{\parallel}$ was noted with increasing mole fraction, $[\text{Li}_2\text{O}]/([\text{Li}_2\text{O}] + [\text{Na}_2\text{O}])$. Kawazoe *et al* (1978c, 1979, 1980b) have applied ESR of Cu^{2+} to the study of immiscibility in $\text{K}_2\text{O-CaO-B}_2\text{O}_3$, $\text{K}_2\text{O-BaO-B}_2\text{O}_3$ and $\text{K}_2\text{O-MgO-B}_2\text{O}_3$ glasses. In the inhomogeneous region, the spectra were found to be superposition of two or three different types of spectra (described earlier) characteristic of representative spectra observed for alkali or alkaline earth borate glasses. The homogeneous region determined by ESR was found to be far wider than that obtained by opalescence in all the three systems. Kawazoe *et al* (1980a) have also studied the rigidity of glass network by analysing the distribution of $g_{\parallel}$ and $A_{\parallel}$ ($\delta g_{\parallel}$ and $\delta A_{\parallel}$) in silicate, borate and phosphate glasses. In similar compositions of $\text{Na}_2\text{O-B}_2\text{O}_3$ and $\text{PbO-B}_2\text{O}_3$ glasses $\delta g_{\parallel}$ was found to be larger for PbO-glass than for $\text{Na}_2\text{O-glass}$ which reflects the difference in the rigidity of these glasses. In another interesting application of ESR of Cu^{2+} in glasses, the mechanism of colouration was investigated by Duran *et al* (1984). They found that both clusters of CuO and crystallites of Cu_2O are present in the glass and the reaction leading to the formation of these products by redox process is suffered by disproportionation reaction involving Sn^{2+} .

Environment of Cu^{2+} in diffusion layers produced by ion exchange in binary alkali-silicate glasses was investigated by Bogomolova *et al* (1983a). They found that isolated Cu^{2+} ions in diffusion layers are in local environments nearly identical with those for Cu^{2+} ions in bulk glasses of the same composition.

5. Concluding remarks

The use of ESR in the investigation of glasses has been increasing steadily in recent years. We have noted in this brief review that substantial amount of work has been done based on ESR of transition metal ions. A certain degree of confidence has emerged with regard to the use of spin Hamiltonian of relevant transition metal ions in ESR studies of glasses. In general ESR parameters and structural geometries appear to possess a reliable degree of correlation. In several instances such as in chalcogenides variation of structures appearing in the glassy matrix are well diagnosed by substantial composition variations of probe ion ESR spectra. Thus the merit of transition metal probe ions in ESR spectral studies of glasses is quite significant.

It is however conspicuous that a number of studies still appear to be more related to the investigation of the ESR behaviour of TM ions in glassy matrices rather than investigation of the structure of glassy matrices using ESR probes. In fact it so happens as

pointed by Griscom that some of the ions like Fe^{3+} exhibit characteristic spectra with minor variations in almost all glassy matrices. TM ions appear to dictate their own local structures in glassy matrices (which we may call as "Griscom effect"). This results in a serious limitation in using transition metal ions as ESR probes. We feel that this tendency is inherently and inversely related to the ionic potential of the probe ion. In other words a low Z/R ion (like Cu^{2+} or Mn^{2+}) is assimilated in the glassy matrix so as to maximize entropy while a high Z/R ion (like Fe^{3+} or V^{4+}) is assimilated such that energy is maximized. It is in the former case which does not lead to 'Griscom effect' that ESR is most useful as a tool for investigating glass structure.

It is disappointing that ESR spectroscopic studies of transition metal ions in glasses have rarely been used to examine the relaxational aspects of such spectra. Parthasarathy *et al* (1982) have investigated the spin-spin relaxation behaviour of Mn^{2+} and Fe^{3+} ions in several glass systems and have arrived at useful correlation between ESR intensities and configurational entropy in the glass transition region.

Acknowledgement

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Electronic structure of spin-mixed iron(III) porphyrins: A proton magnetic resonance study

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Abstract. The proton magnetic resonance studies on the perchlorato iron(III) porphyrins in solution have been described. The isotropic proton shifts in these complexes show anomalous temperature dependence, consistent with its unusual properties in solid state. The NMR data have been analysed on the basis of a crystal field theory which includes lower asymmetric field and spin-orbit interaction. The analysis brings out that the ground state of the ferric ion in these porphyrin complexes exhibits the novel spin-mixed behaviour with spin-mixing between $S = 3/2$ and $S = 5/2$. The ground state is predominantly a spin quartet with the spin sextet being a very close lying excited state. Such a spin situation and spin-mixing have been speculated for the ferric ion in some ferricytochrome *c*'. The present paper also highlights that the isotropic proton shift is very sensitive to the electronic structure of the metal ion and hence can be used to determine the electronic structure of the metal ion in heme systems *in solution*.

Keywords. Proton magnetic resonance; perchlorato iron(III) porphyrins; spin state mixing; crystal field calculations of $1P_1$; electronic structure in solution.

Introduction

The perchlorato iron(III) porphyrins have simple stereochemical structure, in which the iron atom is coordinated to four basal pyrrole nitrogen atoms of the porphyrin ring and to the oxygen atom of the apical perchlorate, completing an approximate 'square pyramidal' stereochemistry around the iron (Reed *et al* 1979; Masuda *et al* 1980). In this respect the gross stereochemistry around the iron in these porphyrin complexes is similar to that of many five-coordinated iron(III) porphyrins which are high-spin (Hoard 1973; Scheidt 1977; Scheidt and Gouterman 1983), with of course some subtle differences as shown in table 1. The most significant difference is that the iron in the perchlorato complexes lies closer to the centre of the mean porphyrin plane, thus making the ligand field at the central metal atom to be stronger. This, together with a weaker axial perchlorate coordination, imparts some remarkable physicochemical properties and makes these perchlorato porphyrin complexes distinctly different from their structurally analogous high-spin ferric porphyrins (Mitra 1983). Some typical magnetic and spectroscopic results on two representative complexes of octaethyl- and tetraphenyl-porphyrins, $\text{Fe}(\text{OEP})\text{ClO}_4$ and $\text{Fe}(\text{TPP})\text{ClO}_4$ respectively, are summarised in table 1 and figure 1.

The detailed solid state magnetic susceptibility, low temperature magnetization and Mössbauer spectroscopy have now confirmed that the ground electronic state of these perchlorato ferric porphyrins is 'predominantly' intermediate-spin state, $S = 3/2$ (Mitra *et al* 1983; Reed *et al* 1979; Dolphin *et al* 1977). This spin state is a rarity among ferric heme complexes and had not earlier been observed in the ferric porphyrins. More

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Table 1. Structural and magnetic properties of the perchlorato iron(III) porphyrins.

Ground spin-state	Temp (°K)	Fe(TPP)ClO ₄	Fe(OEP)ClO ₄	Fe(TPP)Br	Reference
	—	Spin-mixed (predom. $S = 3/2$)	Spin-mixed (predom. $S = 3/2$)	High-spin ($S = 5/2$)	
Fe-N (Å)		2.001	1.994	2.069	Mitra (1983)
Fe-Cl (Å)		0.28	0.26	0.49	{ Reed <i>et al</i> (1979); Masuda <i>et al</i> (1980); Skelton and White (1977)
$\bar{\mu}$ (BM)	290	5.00	4.80	5.85	{ Mitra <i>et al</i> (1983) Behere <i>et al</i> (1979)
	80	4.60	4.20	5.80	
	4.2	3.60	3.50	4.60	
Q.S.	295	2.79	3.16	—	{ Reed <i>et al</i> (1979)
(mm/sec)	4.2	3.50	3.57	—	{ Sams <i>et al</i> (1977)
I.S.*	295	0.30	0.29	—	{ Maricondi <i>et al</i> (1972)
(mm/sec)	4.2	0.38	0.37	0.45	

* Relative to metallic iron.

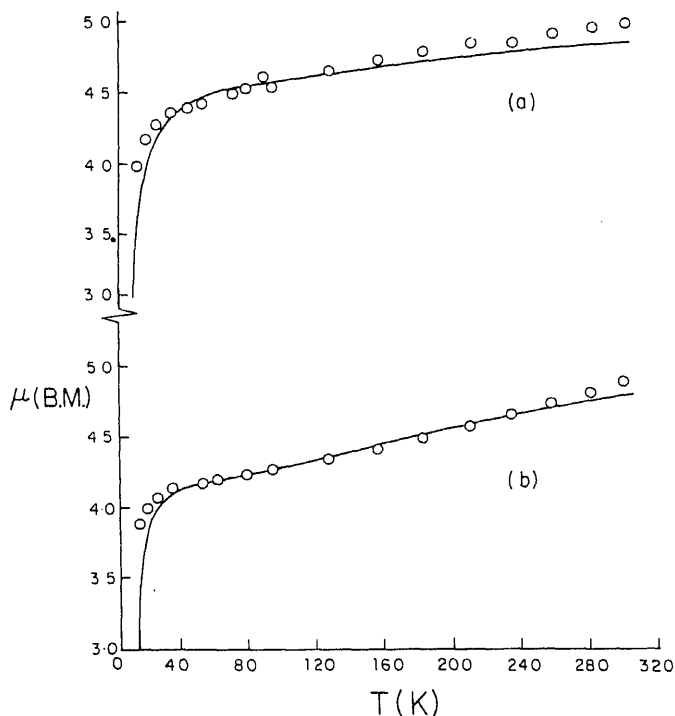


Figure 1. Temperature dependence of the average magnetic moment of (a) Fe(TPP)ClO_4 and (b) Fe(OEP)ClO_4 . The solid curves are theoretically calculated ones.

significantly, it was established that the ground state was quantum-mechanically spin-mixed, which was responsible for their novel physicochemical properties (Mitra *et al* 1983; Mitra 1983). Such spin state mixing of the ground state was predicted several years ago for the ferric hemes (Harris 1968) but definite experimental evidence was lacking. The perchlorato ferric porphyrins were thus the first example of truly spin-mixed ground state in synthetic metalloporphyrins.

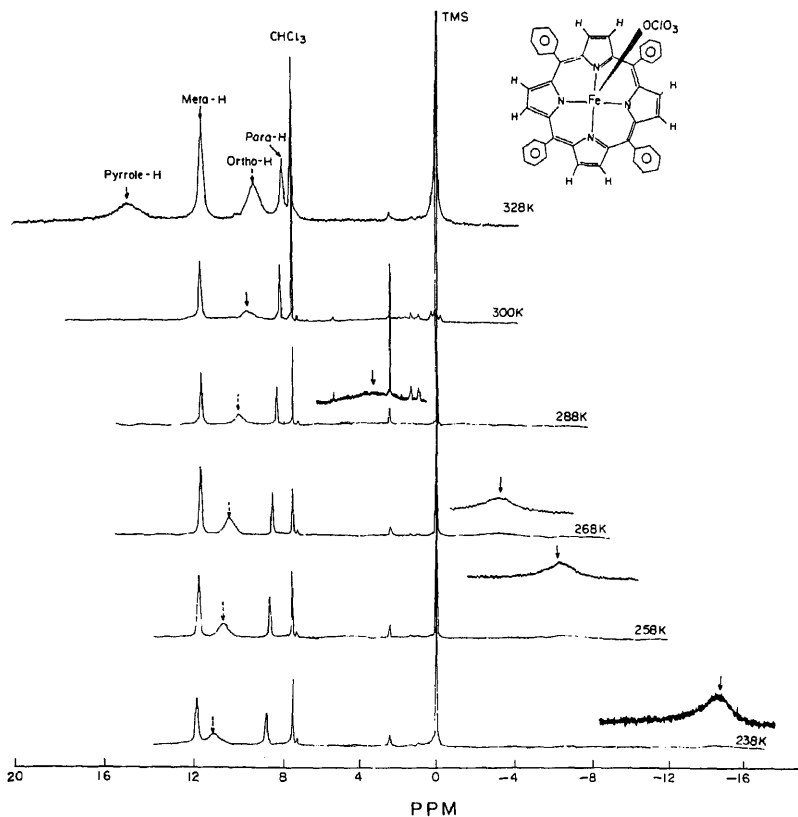
The electronic structure of these molecules is thus of considerable interest as it is possible for their 'anomalous' physical properties. A question of importance is to determine if these properties are entirely intramolecular and if the spin-mixed ground state and electronic structure of these molecules are retained in solution. Such information can be obtained from the analysis of the variable temperature NMR studies of these metalloporphyrins in solution (Dugad and Mitra 1984). In the present paper we discuss the variable temperature proton magnetic resonance (PMR) studies in solution on the Fe(TPP)ClO_4 and Fe(OEP)ClO_4 and analyse the isotropic proton shift in terms of a crystal field model for d^5 electron configuration.

Experimental

deuterated chloroform and in benzene. During the variable temperature measurements, the temperatures were held constant within $\pm 1.0^\circ$. The results of measurements are shown in figures 2-4. In all our work down-field chemical shifts have been taken as positive.

3. Theoretical model

The theoretical crystal field model used here has earlier been elaborated elsewhere (Marathe and Mitra 1976). Only essential features are therefore discussed here. In the model a tetragonal symmetry of the crystal field is assumed, which is generally valid for metalloporphyrins. In a crystal field of tetragonal symmetry, the five d -orbitals of the ferric ion would split into three orbital singlets and one orbital doublet denoted as $b_1(x^2 - y^2)$, $a_1(3z^2 - r^2)$, $b_2(xy)$ and $e(xz, yz)$ respectively. The relative energies of these orbitals can be given by three parameters Δ , δ_1 and δ_2 defined in figure 5. For the complexes with axial ligand weaker compared to the equatorial one (as in these metalloporphyrins), δ_1 can both be positive or negative but δ_2 is always positive and much larger than δ_1 . When the five d electrons are filled in these orbitals, either a spin



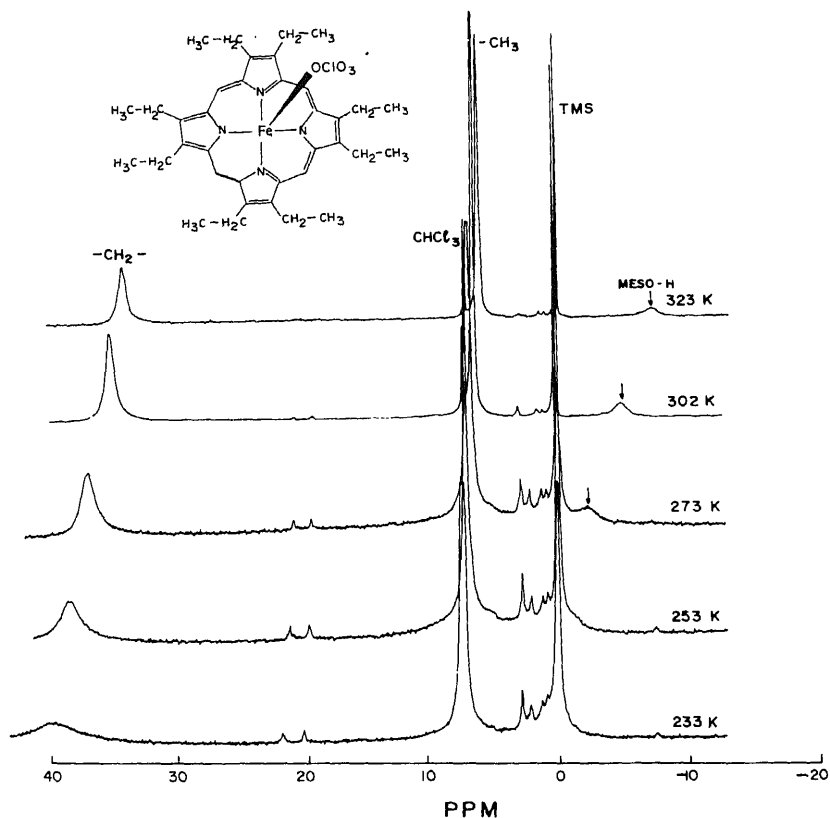


Figure 3. Temperature dependence of the 1H NMR spectra for the Fe(OEP)ClO₄ in CDCl₃. Note that only one resonance for the CH₂ protons is observed.

et or doublet or quartet stabilises as the ground state depending on the values of Δ , δ_2 and the Racah parameters, B and C . Table 2 lists the states and their relative energies, which merit consideration as possible ground and low-lying excited states for ferric porphyrins.

Using spin orbitals given by Griffith (1964) the five d electron wave functions in the form of Slater determinants were formed. The set of twenty-four wave functions corresponding to the five states (6A_1 , 4A_1 , 4E , 2E , 2B_2) were calculated. Using these wave functions as a basis set, 24×24 matrix elements of the spin-orbit coupling and magnetic interactions were calculated using the operator

$$H = \zeta \sum_{i=1}^5 \mathbf{l}_i \cdot \mathbf{s}_i + \beta \mathbf{H} \cdot \sum_{i=1}^5 (\mathbf{l}_i + 2\mathbf{s}_i),$$

where ζ is the spin-orbit coupling parameter. This matrix along with the energies of different configurations was then used for calculating the expectation values, $\langle S^2 \rangle$, $\langle AS \rangle$ etc. Calculations were performed for various orientations of

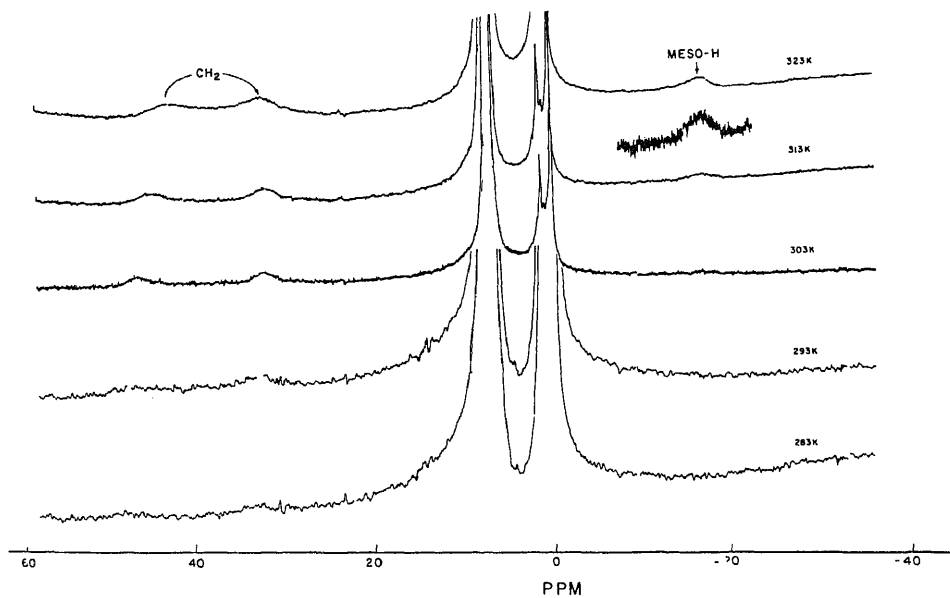


Figure 4. Temperature dependence of the NMR spectra for the Fe(OEP)ClO₄ in deuterated benzene. Note the two resonances for the CH₂-protons, which are broad.

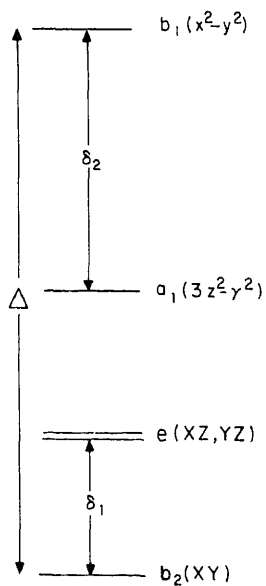


Table 2. Interelectronic repulsion and tetragonal ligand field energies of the sextet, quartet and doublet states of a d^5 ion.

Configuration	Energy (w.r. to 6A_1)
$(b_2e^2a_1b_1)$	$E_1 = 0$
$(b_2^2e^2a_1)$	$E_2 = 10B + 6C - \Delta$
$p\{b_2e^3a_1\} + q\{b_2e^3b_1\}$	$E_3 = [\{14B + 6C - \Delta + \delta_1 + \delta_2/2\} - \{(2B - \delta_2/2)^2 + 12B^2\}^{1/2}]$
$(b_2^2e^3)$	$E_4 = 15B + 10C - 2\Delta + \delta_1 + \delta_2$
(b_2e^4)	$E_5 = 15B + 10C - 2\Delta + 2\delta_1 + \delta_2$

$$-q^2 = 1.$$

In order to consider whether hyperfine coupling constants (A) differ significantly for different spin states, the paramagnetic contact shifts were calculated using the relation

$$(\Delta H/H)_{CS} = -\frac{\langle AS \rangle}{g_N \beta_N H}$$

while the dipolar shift was calculated using the conventional formula (Mitra 1977)

$$(\Delta H/H)_{DS} = \left(\frac{3 \cos^2 \theta - 1}{r^3} \right) (K_{\perp} - K_{\parallel}).$$

where r is the length of the vector between the nucleus under study and the metal ion, and θ is the angle which this vector makes with the symmetry axis of the molecule. $K_{\parallel}$ and $K_{\perp}$ are the molecular susceptibilities parallel and perpendicular to the molecular symmetry axis.

Results

Several features of the experimental results in figures 2–4 are noteworthy. The most striking among them is the ‘anomalous’ temperature dependence of the iPS for the pyrrole proton in the Fe(TPP)ClO₄ complex (figure 2), which has also been observed previously (Goff and Shimomura 1980). In the OEP complex the temperature dependence of the CH₂ proton is not equally marked but the meso-proton isotropic shift does show a similar ‘anomalous’ temperature dependence. The theory of iPS in transition metal complexes shows that a $1/T$ (or only a small departure from $1/T$) temperature dependence is expected for orbitally non-degenerate ground state with any discrete spin-state. This has been experimentally verified for the large body of transition metal complexes including metalloporphyrins (LaMar and Walker 1979; Behere *et al* 1982; Dhingra *et al* 1975; Dugad and Mitra 1984). In the two perchlorato porphyrin complexes the iPS shows no similarity to a $1/T$ dependence for the pyrrole and other protons, and suggests that the ground state may not be a pure discrete spin-state. A similar conclusion has been derived from the solid state magnetic measurements (figure 1) and supports the view that the ‘anomalous’ magnetic and electronic properties exhibited by the two perchlorato iron(III) porphyrins are intramolecular in origin. It is therefore expected that an analysis of the iPS data may lead to information

Before we attempt a theoretical analysis, we digress and discuss another feature of the results, as shown in figure 4. The proton NMR spectra of both the compounds in deuterated benzene are quite different from those in CDCl_3 . The spectrum of the TPP compound is too broad in the temperature range to merit any further remark but that of the OEP compound is interesting. The difference from the CDCl_3 spectrum lies not only in that two resonances (instead of a single one as in CDCl_3) for the CH_2 protons are observed but also in that the IPS for the both CH_2 and meso-H (which is much too poorly resolved) shows a different temperature dependence in C_6D_6 . In CDCl_3 the two CH_2 protons would be rotating fast making them magnetically equivalent with respect to the iron atom, and only one resonance is observed. On the other hand, the motion of CH_2 protons in an aromatic solvent like benzene is expected to be hindered and slow (on the NMR time scale) making the two protons magnetically inequivalent, and hence the two resonances. At higher temperatures the motion would become less restricted, and the CH_2 proton may rotate freely giving single resonance. While the experimental results in figure 4 do not go upto such high temperature the trend is clear. The difference in the temperature dependence of the CH_2 and meso protons in C_6D_6 is reminiscent of the effect of aromatic solvents on the IPS in many other metal-porphyrins (Fulton and LaMar 1976).

5. Analysis of the experimental data

Analysis of the IPS on the basis of the theory outlined in §3 involves several parameters, namely ζ , Δ , δ_1 , δ_2 and A 's. The first four parameters are also involved in the calculation of the magnetic moment and hence must be chosen so as to be consistent with the temperature dependence of both sets of the experimental results. The number of parameters is however too large to be uniquely decided from the present results. It is therefore necessary that we find out the relative sensitivity of the parameters to the $\bar{\mu}$ and IPS, and define region of possible fits.

Exploring the regions of parameter space which would be of interest for the present discussion, we find that Δ and δ_1 must lie in a limited region such that $36,000 > \Delta > 33,000 \text{ (cm}^{-1}\text{)}$ and $5000 > \delta_1 > 1500 \text{ (cm}^{-1}\text{)}$. For values of Δ and δ_1 outside these limits the ferric ion moves out of the region of interest and goes into either high- or low-spin regions, which are evidently not acceptable. In figures 6–8, the dependence of $\bar{\mu}$ on Δ , δ_1 and ζ over a wide range of temperature is shown. Clearly $\bar{\mu}$ is very sensitive to Δ while it is largely insensitive to changes in δ_1 . Changes in δ_2 have likewise hardly any effect on $\bar{\mu}$ (and the IPS). The effect of ζ on the $\bar{\mu}$ is interesting. While the $\bar{\mu}$ at room temperature is not much sensitive to small changes in ζ its temperature dependence especially at low temperatures shows subtle differences.

Figures 9–11 show similar dependence of the IPS on Δ , δ_1 and ζ in the temperature range of the NMR measurements. For the purpose of this analysis, pyrrole proton of the TPP complex was chosen for its unique variation. Like the $\bar{\mu}$, the IPS shows similar large changes with even small changes in Δ , and very little change with δ_1 . The variation in ζ affects the magnitude of the IPS but not its temperature dependence. Figures 9 and 10 show that the present theoretical calculation is able to reproduce closely the 'anomalous' features in the temperature dependence of the experimental IPS of the

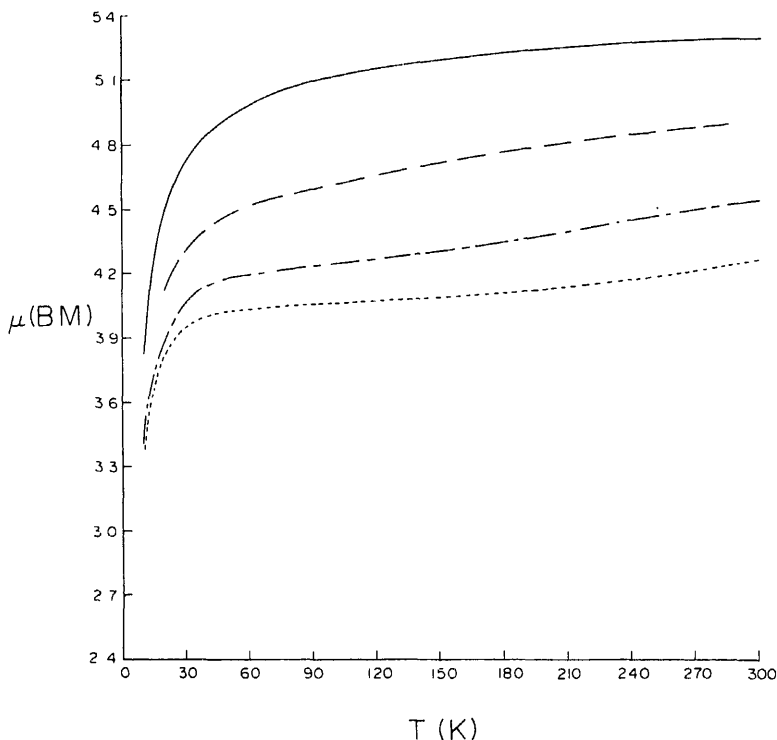


Figure 6. Temperature dependence of $\bar{\mu}$ for various values of Δ : —, $\Delta = 33,900 \text{ cm}^{-1}$; — — —, $\Delta = 34,100 \text{ cm}^{-1}$; - - -, $\Delta = 34,300 \text{ cm}^{-1}$ and ····, $\Delta = 34,500 \text{ cm}^{-1}$. ζ and δ_1 were held at 200 and 2500 cm^{-1} respectively.

We investigate next the dependence of the ips on the hyperfine coupling constants. Here we consider the A values corresponding to only 6A_1 and 4A_2 as these two states appear to be the only low-lying ones and significantly contribute to the ips. Figures 12 and 13 show the effect for various combinations of the A values. The sign of the ips is dependent on the sign of the A values. Also, the magnitude of the ips is much higher when the signs of the A are similar than when they are opposite.

Summarising the results, the following observations emerge from the above investigations. There is a limited region of parameter space delineated by Δ and δ_1 , which seems to describe the magnetic and NMR properties of the two perchlorato compounds. In this parameter region the ips is very sensitive to Δ , ζ and A , and the calculations are capable of reproducing the essential features of the proton NMR results, including the unusual temperature dependence of the ips of the pyrrole proton in the TPP complex. The ips and $\bar{\mu}$ are not sensitive to the δ_1 and δ_2 in the range of their values of present interest. All these observations are important in the least-square fitting of the data, since the general strategy for the best-fit procedure would be to fix the less sensitive parameters at some reasonable value and vary the parameters which have large effect on the experimental results.

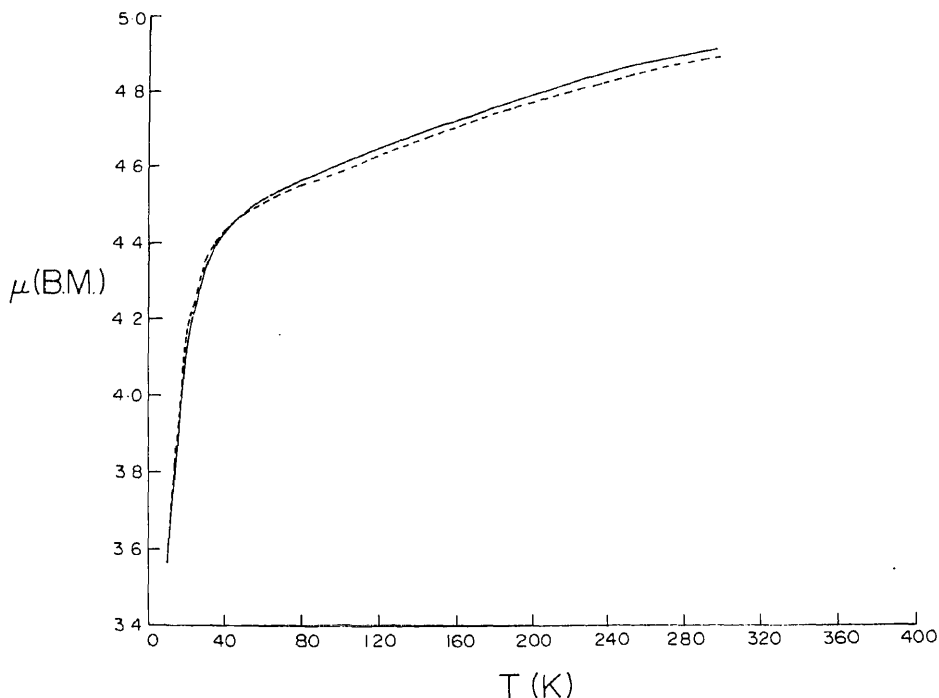


Figure 7. Temperature dependence of $\bar{\mu}$ for various values of δ_1 , —, $\delta_1 = 2500, 5000 \text{ cm}^{-1}$; --, $\delta_1 = 1500 \text{ cm}^{-1}$. Here Δ and ζ were held at $34,100$ and 200 cm^{-1} respectively.

temperature. The fits are shown in figure 1 for the $\bar{\mu}$ and figures 14 and 15 for the μ_{PS} results. In the fitting procedure δ_1 was kept at 2500 cm^{-1} and $\delta_2 = 10 \delta_1$. Since δ_2 is expected to be much larger than δ_1 and almost insensitive to both the $\bar{\mu}$ and μ_{PS} , such a choice for δ_2 was made. Table 3 includes the crystal field parameters deduced from the best-fit procedure.

6. Discussion

Using the crystal field parameters listed in table 3, the values of $g_{\parallel}$, $g_{\perp}$, ground state wave functions and energies of low-lying states were determined (tables 3 and 4). These values are not much affected by the uncertainties in the determination of δ_1 and δ_2 , and are reasonably reliable. The results confirm that the ground state is a spin-mixed state with predominant spin-quartet character. The spin-sextet (6A_1) is the lowest lying excited state though an elaborate search indicated a spin-doublet (2E) to be the next excited state over 1000 cm^{-1} above the ground state. We have therefore excluded it from our discussion. The mixing-in of the spin-sextet is more in the TPP complex, which is consistent with its higher room temperature magnetic moment.

The calculated g -values in table 3 refer to that of the ground state. The 4A_2 state splits into $M_{\text{eff}} = 1/2$ and $M_{\text{eff}} = 3/2$ with g -values of 2.0 and 2.4 respectively. The 4E state

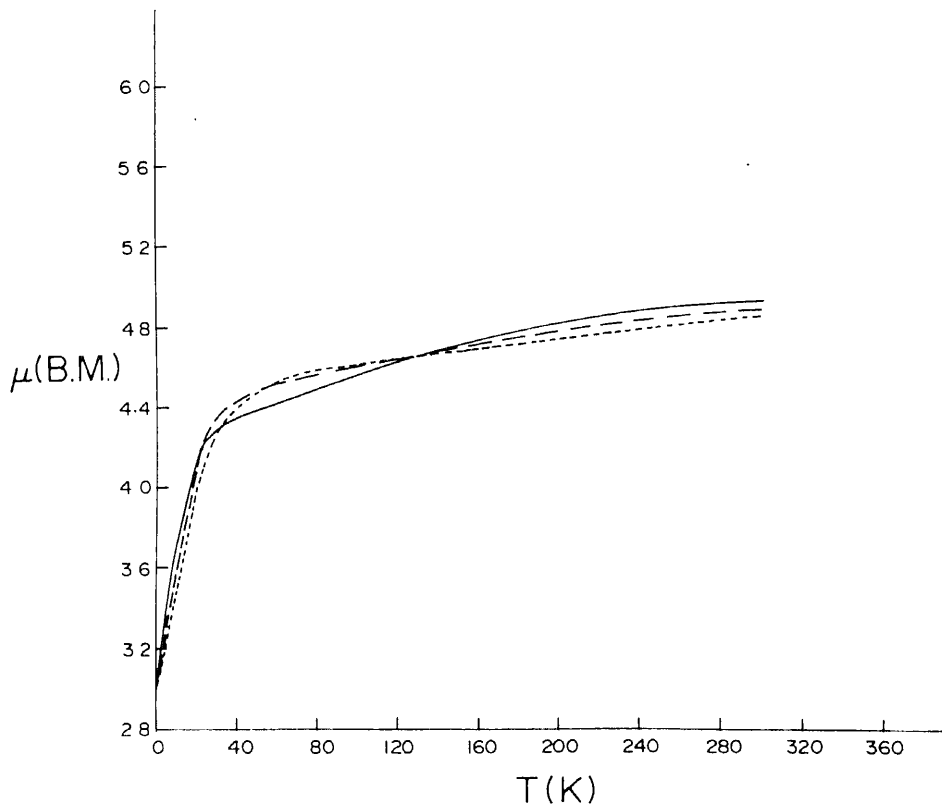


Figure 8. Temperature dependence of $\bar{\mu}$ for various values of ζ : —, $\zeta = 100 \text{ cm}^{-1}$; — —, $\zeta = 200 \text{ cm}^{-1}$ and - - - , $\zeta = 300 \text{ cm}^{-1}$. Here Δ and δ_1 were held at $34,100$ and 2500 cm^{-1} respectively.

$g_{\parallel} = 2.0$ and $g_{\perp} = 4.0$. The effect of spin-mixing with the excited zero-field states of the 6A_1 is to increase the $g_{\perp}$ while $g_{\parallel}$ remains unaffected. This is reflected in the calculated g -values for the two complexes, showing considerable enhancement in the $g_{\perp}$ value. An ESR measurement (Reed *et al* 1979) carried out on the $\text{Fe}(\text{TPP})\text{ClO}_4$ at 10 K has given $g_{\parallel} = 2.03$ and $g_{\perp} = 4.75$, in close agreement with the calculated ones.

The values of ζ for both the complexes are considerably lower than the free-ion value of 460 cm^{-1} . Similar low values have been obtained in other spin-mixed ferric porphyrins (Mitra 1983; Gunter *et al* 1984). While reduction in value of ζ is generally attributed to covalency, it is apparent that such a large reduction is unlikely to be due to covalency alone. It is possible that it may in part be due to the limitation in the theory as applicable to such systems.

The electronic structure of the perchlorato ferric porphyrins having a spin-mixed ground state with predominant spin-quartet character has several interesting implications. Firstly, it establishes that such a spin-situation is possible for heme systems with weak axial ligation, though its existence had earlier remained unidentified

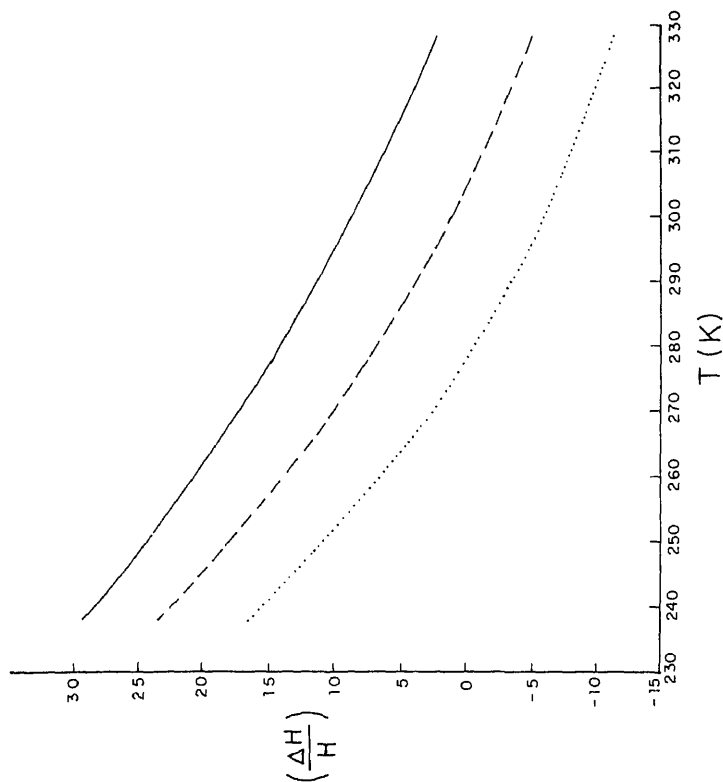


Figure 10. Temperature dependence of the ips with varying ζ : —, $\zeta = 300\text{cm}^{-1}$; ---, $\zeta = 200\text{cm}^{-1}$ and, $\zeta = 100\text{cm}^{-1}$. Δ and δ_1 were held at 34,100 and 2500 cm^{-1} respectively. Note that the ips changes sign with temperature for ζ

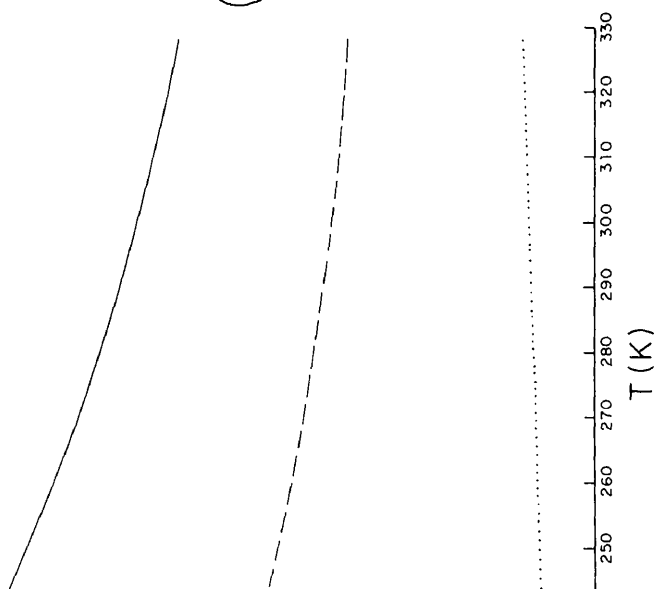


Figure 11. Temperature dependence of ips for various values of Δ : —, $\Delta = 34,000\text{cm}^{-1}$; ---, $\Delta = 34,100\text{cm}^{-1}$ and, $\Delta = 34,200\text{cm}^{-1}$. Note that for $\zeta = 300\text{cm}^{-1}$ and $\delta_1 = 2500\text{cm}^{-1}$, the ips changes sign with temperature as is experimentally observed in

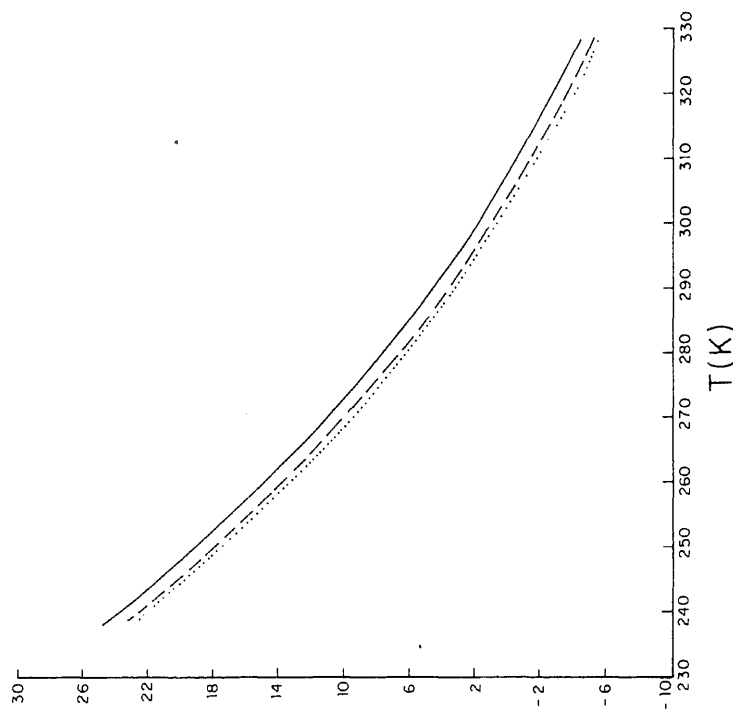


Figure 11. Temperature dependence of the ips with varying δ_1 : —, $\delta_1 = 3000 \text{ cm}^{-1}$; ---, $\delta_1 = 2500 \text{ cm}^{-1}$ and . . . , $\delta_1 = 200 \text{ cm}^{-1}$ and . . . , $\delta_1 = 100 \text{ cm}^{-1}$ respectively. All other parameters are held constant, see table 3.

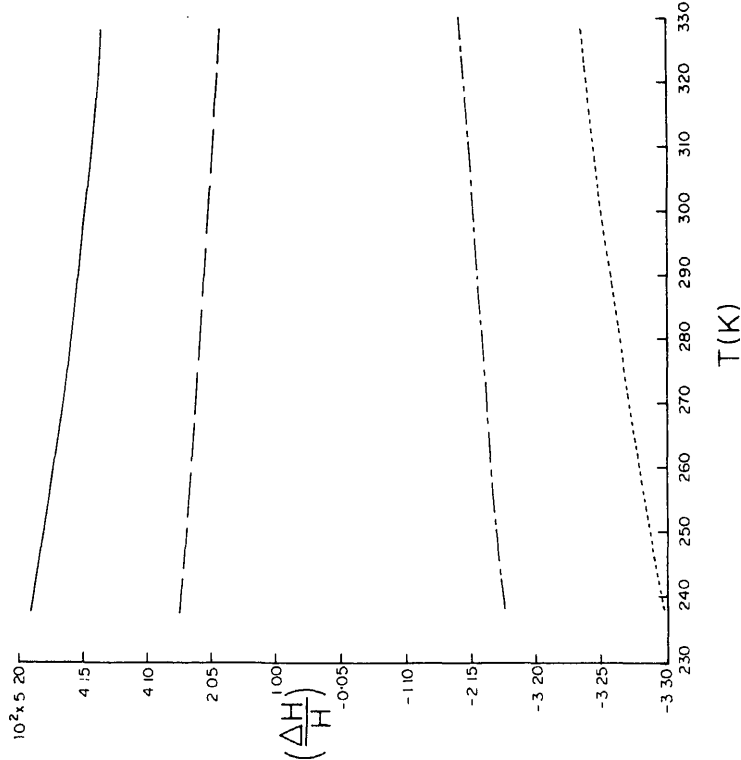


Figure 12. Temperature dependence of the ips with varying A values: —, $A(5/2) = -2.0$; ---, $A(5/2) = -1.0$; . . . , $A(3/2) = -1.0$; - - - , $A(3/2) = -1.0$. Note the difference in the scale for the ips. All other parameters are held constant, see table 3.

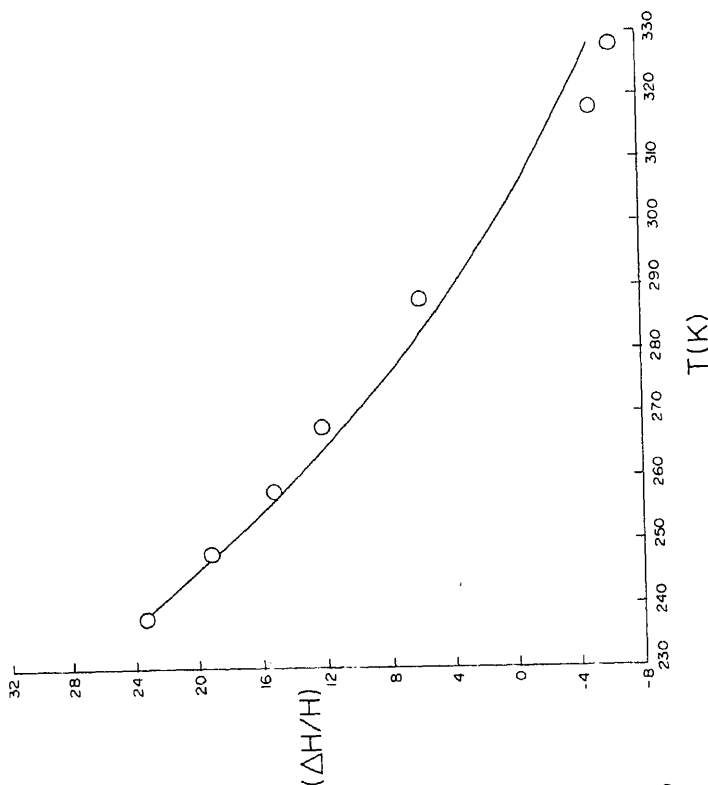


Figure 14. Temperature dependence of the pyrrole IPRs in Fe(TPP)ClO_4 . The circles are experimental data from figure 2 and the solid curve is the calculated one for parameters given in table 3.

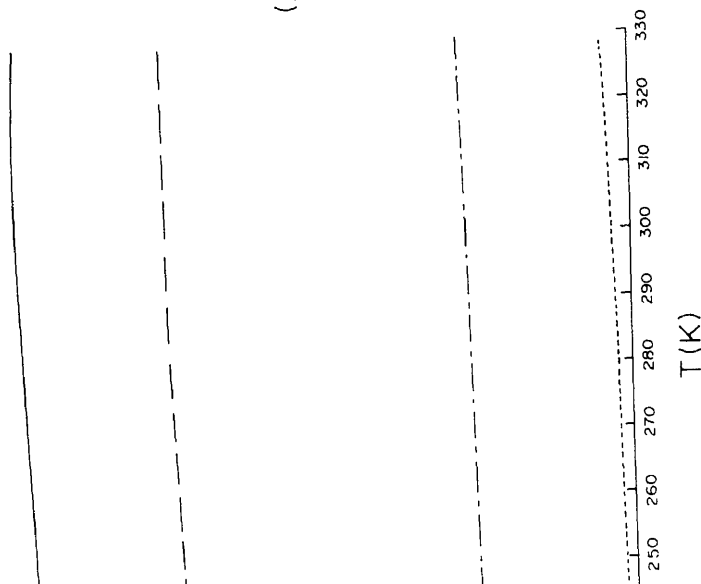


Figure 15. Temperature dependence of the IPRs with varying A : — $A(5/2) = -2.0$, - - $A(5/2) = -1.0$, $A(3/2) = +1.0$; - . - $A(5/2) = +1.0$, . . . $A(5/2) = +2.0$, $A(3/2) = -2.0$. All the values are in MHz. Parameters are held constant at appropriate values shown in table 3.

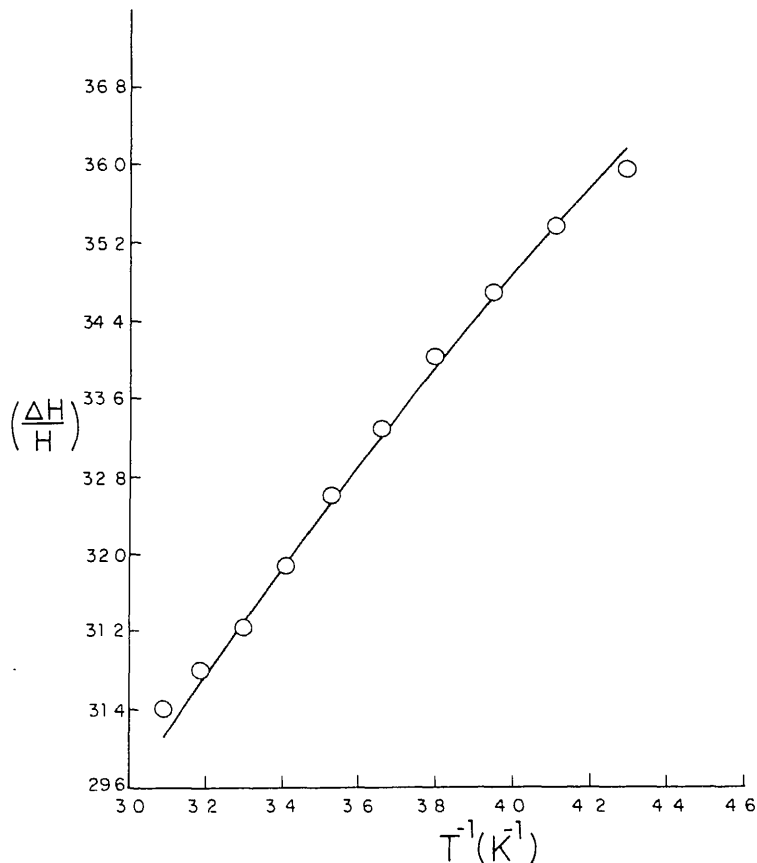


Figure 15. Temperature dependence of the IPS for the CH_2 proton in $Fe(OEP)ClO_4$. The circles are the experimental data from figure 3 and the solid curve is the calculated one for parameters given in table 3.

Table 3. Crystal field parameters and ground state properties for $Fe(TPP)ClO_4$ and $Fe(OEP)ClO_4$.

Crystal field and other parameters	$Fe(TPP)ClO_4$	$Fe(OEP)ClO_4$
Δ	$34,100 \text{ cm}^{-1}$	$34,200 \text{ cm}^{-1}$
ζ	200 cm^{-1}	120 cm^{-1}
δ_1^*	2500 cm^{-1}	2500 cm^{-1}
$g_{ }$	2.0	2.0
$g_{\perp}$	4.77	4.39
Ground state	4A_1 , 61%	4A_1 , 80%

Table 4. Energies of the low-lying states in Fe(TPP)ClO₄ and Fe(OEP)ClO₄.

States	Fe(TPP)ClO ₄	Fe(OEP)ClO ₄
	Energies (cm ⁻¹)	Energies (cm ⁻¹)
⁴ A ₂ ± 1/2 >*	0	0
⁴ A ₂ ± 3/2 >*	38	18
⁶ A ₁ ± 5/2 >	275	264
⁶ A ₁ ± 3/2 >*	405	313
⁶ A ₁ ± 1/2 >*	445	332

All energies are relative to the ground state ⁴A₂ | ± 1/2 >. The spin-admixed states are designated by asterisk.

rather limited experimental data. Now that extensive physical measurements on the synthetic porphyrins both in solid and solution have established clearly the detailed features of the properties of such ground state, the results on the cytochrome *c'* do appear clearly indicative of the similarly spin-mixed predominant spin-quartet ground state. This raises an intriguing question as to the mode of the axial ligation in the cytochrome *c'* leading to this ground state. All available structural data on the cytochrome *c'* are consistent with a five coordinate heme having a single axial histidine, with the sixth position being unoccupied (Spiro *et al* 1979). The axial analogy with the perchlorato porphyrins indicates that for the cytochrome *c'* to show similar ground electronic state properties, the axial ligand field should be similar to that of the perchlorate ion. There is a suggestion (Reed *et al* 1979) that fission of the Fe-N_{hist} bond and coordination to a weak ligand anion oxygen donor in the other axial site could give rise to this situation. Such a possibility has been documented in a mutant hemoglobin where a distal tyrosinate rather than the normal proximal histidine is coordinated to the ferric ion in the Hb Boston (Pulsinelli *et al* 1973).

7. Conclusion

The present proton NMR study has highlighted several points which are summarised below.

(i) The perchlorato iron(III) porphyrins show anomalous properties in solution, which are similar to those in the solid state. The origin of these properties is therefore intramolecular and lies in the novel properties of the ground electronic state.

(ii) The ground electronic state of these molecules is spin-mixed with a predominant spin-quartet character. Such a ground state is a rarity in both natural and synthetic hemes, and has been speculated in certain bacterial ferric cytochrome *c'*.

(iii) The *g* factors and its temperature dependence is observed to be sensitive to the properties and characteristics of the ground and lowlying excited states. A careful and accurate NMR study therefore promises to be useful to understand the electronic structure of the heme metal ion in solution. This is particularly of significance as the method can be extended to the study of the electronic structure in paramagnetic heme

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Abstract. Recent trends in the field of ion bombardment of material surfaces are reviewed with a brief discussion about the present understanding of the subject. The use of novel characterization concepts to explore the ion beam-induced phenomena is emphasized and in this context the importance of the technique of conversion electron Mössbauer spectroscopy (CEMS) is brought out. A number of specific examples of the use of CEMS technique to studies on ion implantation, ion beam mixing and corrosion of ion-bombarded surfaces have been given.

Keywords. Mössbauer spectroscopy; ion bombardment; ion implantation; material surfaces.

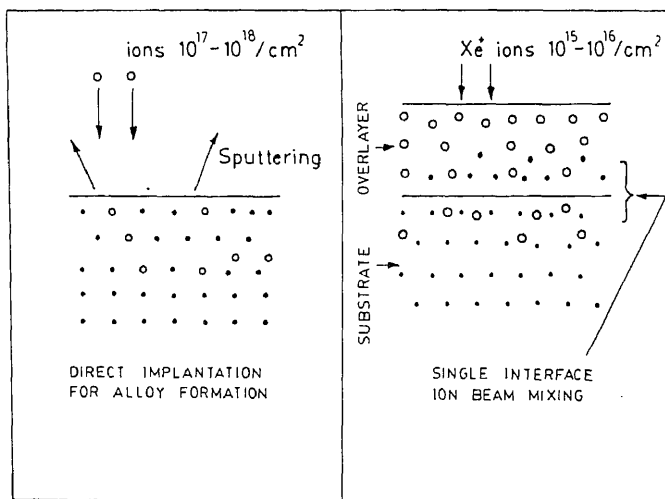
1. Introduction

In recent years there has been an enormous growth of research activity in the field of materials science. The major attention of this activity is focussed on the question of obtaining material surfaces tailored to required specifications (Poate *et al* 1978, 1981; Gibbson *et al* 1981; White and Peercy 1980). The conventional techniques of equilibrium thermal treatment either for alloying, annealing or impurity diffusion cannot offer a useful solution to this problem because of various reasons which have been detailed elsewhere; the important one being the difficulty of adaptation due to non-availability of suitable process parameters. Hence during the past decade there has been considerable growth of interest in the use of radiation processing methods to obtain suitably tailored surfaces (Carter and Colligon 1968; Mayer *et al* 1970; Crowder 1973; Poate *et al* 1981; Hoonhaut 1981; Sood 1982). Amongst the radiation processing techniques generally employed, the prominent ones are ion implantation, ion beam mixing, laser treatment, electron beam treatment etc. In the present article we shall only discuss those techniques which are based on the use of energetic ion beams for processing of material surfaces.

The basic ion beam method of surface modification is ion implantation, in which selected ionic species having energy in the range of a few tens to a few hundreds of keV are bombarded on solids (Carter and Colligon 1968; Mayer *et al* 1970; Crowder 1973). This is a high vacuum (10^{-6} torr) process which offers a possibility of obtaining a specific dopant distribution in the submicron region below the solid surface by controlling the ion energy, target temperature, orientation of the target structure with reference to ion direction etc. Since the implantation energies used in most experiments are in the keV range, the atoms of solid which are displaced from their sites by the incoming ions also possess substantial energy to atomically displace other atoms on their track. Such sequential scattering events generate a zone in the neighbourhood of the track of the incoming ion, which is often referred to as a 'collision cascade region' (Poate *et al* 1981). The cascade formation occurs over a time scale of only 10^{-13} to 10^{-10} seconds rendering a highly non-equilibrium nature to the implantation process

and thus offering a possibility of synthesizing metastable surface alloys and solid solutions. This aspect is especially important in the context of metals, and metal-semiconductor systems, wherein one desires to obtain newer metastable solid solutions with novel application potentials. The process of direct implantation is however not suitable in applications which require high-concentration alloys because synthesis of such alloys requires bombardment at ion dose values as high as 10^{17} – 10^{18} ions/cm², and at such dose values the sputtering effect (Carter and Colligon 1968) erodes the presynthesized alloy layers. Thus it becomes necessary to find out alternative non-equilibrium methods of producing such metastable alloys in thin film form. It was shown by Tsaur *et al* (1979) that a simple but interesting variation of ion implantation method itself can be used to synthesize concentrated metastable alloys on the surface of any material without the intrinsic limitation imposed by the sputtering effect in the direct implantation case. This innovation is referred to as ion beam mixing.

The principle of ion beam mixing is depicted in figure 1. This technique is based on the fact that an energetic ion incident on a solid surface can dynamically move nearly hundred or more of the atoms of the surface layers over many lattice distances. Hence an ion dose of 5×10^{15} ions/cm² can lead to a dynamical mixing of 10^{17} to 10^{18} atoms in the surface layers of a solid. If these layers are composed of successively deposited thin films, an atomic mixing of these films can take place yielding a homogeneous high concentration alloy. Since the dose required to achieve alloying is almost two orders of magnitude lower in the case of ion beam mixing than that required in the direct implantation process, the sputtering limitation of the latter method is almost completely eliminated (Poate *et al* 1981). Also in view of the small dose, the percentage of the implanted ions in the composition of the mixed alloy is extremely small and thus beam mixing can be carried out by using any suitable ions of chemically inert gaseous species such as Ar⁺, Kr⁺, Xe⁺ etc with little risk of influencing the physical properties of the alloy. It may further be observed that since the basic process used in ion beam



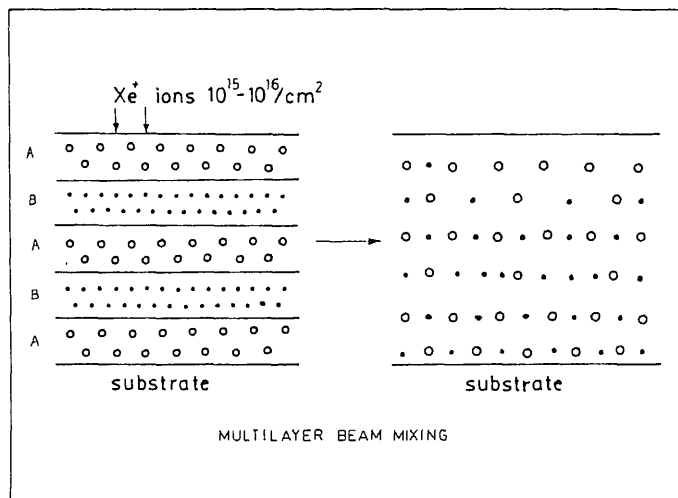


Figure 2. Ion beam mixing process in the case of a multilayered structure.

mixing is ion implantation itself, it preserves the most important advantage of the implantation method, *viz* its highly non-equilibrium nature which can lead to novel metastable structures and compositions. Also, the technique of ion beam mixing can be used effectively to tailor the composition of the mixed layer (figure 2). This can be achieved by preparing a layered structure of alloying elements having thicknesses suitable to yield specific final composition and subsequently mixing the deposited multilayered sandwich by energetic inert gas ions. In this multi-interface case, the energy of ions used to achieve mixing may be varied over a chosen range.

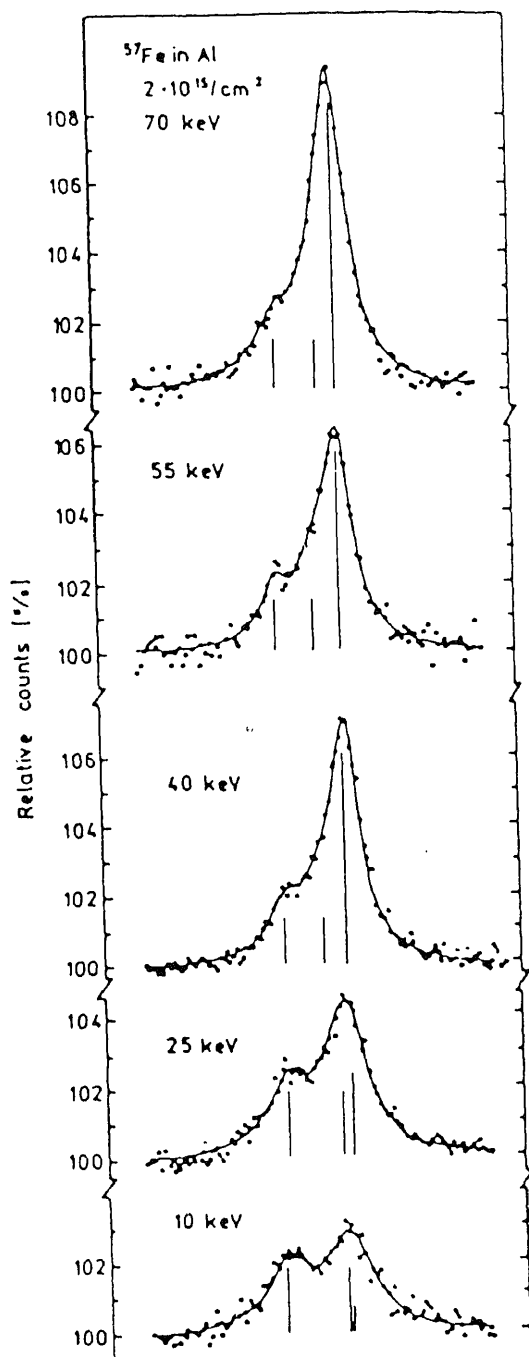
Considerable experimental work has already been done (Carter and Colligon 1968; Mayer *et al* 1970; Crowder 1973) in the area of ion bombardment of solids to understand the physical processes which can occur when radiation of a specific type is incident on the material surface. In most of these studies the techniques of Rutherford backscattering (RBS), x-ray diffraction (XRD), resistivity measurements etc have been employed and valuable information regarding the structural and chemical properties of processed layers has been obtained. Yet a need is felt for additional data, especially on the atomistic aspects of the beam-induced processes to understand the finer details of the nature and properties of the new materials which can be synthesized by the beam processing techniques. Amongst the characterization techniques which can directly address to the atomic level details, the technique of Mössbauer spectroscopy has a special place because, it can, in a single measurement, throw light on the structural, chemical, electrical and magnetic properties of materials as well as give valuable data on the defect complexes and their symmetries. Also this technique, being non-destructive in nature, does not forbid the use of other characterization concepts for studying the same material. Thus a coherent picture regarding the state of solid can be obtained without difficulty. Mössbauer spectroscopy provides a number of windows such as isomer shifts, quadrupole splitting, magnetic dipole interaction, Lamb-

the non-Mössbauer accessible materials can also be studied by this method.

The technique of Mössbauer spectroscopy can either be used in transmission mode or in scattering mode depending upon the need of the investigation. The scattering geometry, especially the one employing detection of conversion electrons emitted by the Mössbauer nuclei subsequent to gamma absorption, is particularly suited for studies of ion-irradiated surfaces because one can obtain Mössbauer information selectively from the submicron region below the solid surface which is primarily affected by the ion bombardment process (Sawicka and Sawicki 1981). In the case of iron (^{57}Fe) the energy of conversion electrons is ~ 7.3 keV and as such the electrons emitted within a depth of $0.25\ \mu\text{m}$ can only emerge out of the surface and be detected. The conversion electrons emitted from the sample surface are generally detected in a gas ($\text{He} + 4\%$ ethanol mixture) flow type of proportional counter in an integral manner and the Mössbauer information regarding the surface layers is obtained. Other detection schemes such as the ones employing channeltron type of detectors can also be employed but these are more sophisticated and expensive. In what follows we describe some results of conversion electron Mössbauer spectroscopic (CEMS) studies carried out on ion bombarded surfaces using simple gas flow type of proportional detectors.

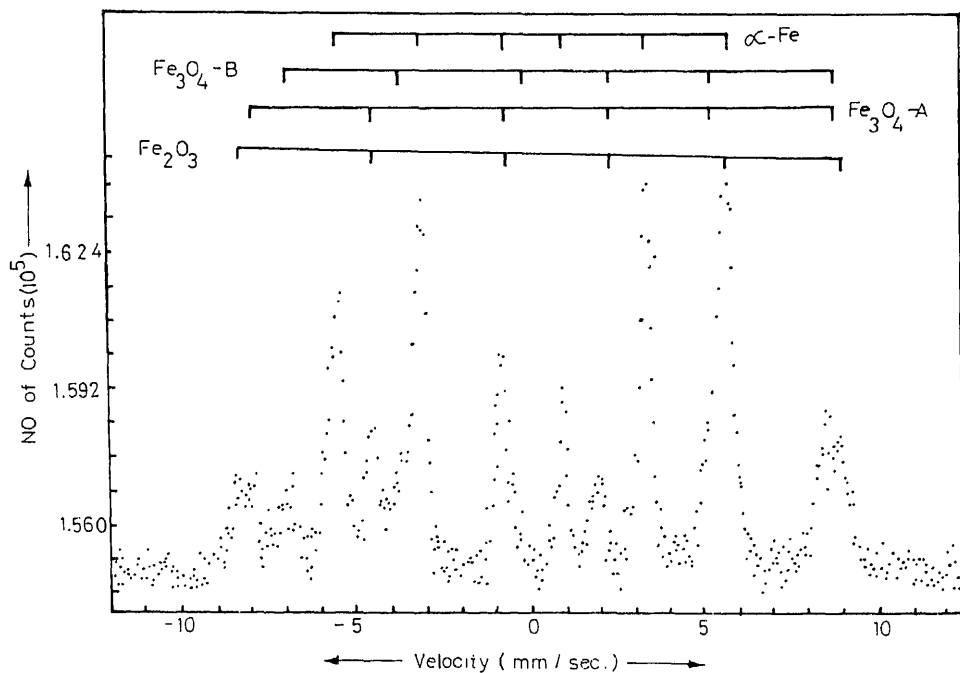
2. Ion implantation: CEMS study

Sawicka and Sawicki (1981) studied the ^{57}Fe -implanted Al, Si, Ge and diamond samples using CEMS technique. In the case of aluminium host, the effects of ^{57}Fe implantation were studied (Sawicka *et al* 1978) over an ion dose range of 10^{14} ions/ cm^2 to 2×10^{17} ions/ cm^2 . The maximum average ion concentration attained in aluminium is $\sim 30\%$, which is far above the solubility limit of iron in aluminium (0.001% at room temperature and 0.025% at 650°C). Some results of CEMS measurements on ^{57}Fe implanted in aluminium are given in figure 3. The CEM spectra indicate a systematic variation of spectral features with change in the average iron concentration and this is irrespective of whether the concentration is achieved by variation of energy or dose. At iron concentrations smaller than 5% the spectra are composed of a singlet and a quadrupole split doublet. The single line can be attributed to iron monomers, while the doublet to higher iron associations (especially dimers) (Nasu *et al* 1980). As the average iron concentration is increased upto 5% the contribution of the single line decreases while that of the doublet increases systematically. The values of isomer shift corresponding to the two contributions show that the s-electron density at Fe-nucleus is larger in iron dimers than in monomers. In this case the CEMS technique also reveals that the iron aggregation process is enhanced both by implantation at high doses (leading to high defect concentrations) and by thermal treatment. In fact, the fast quenching nature of ion implantation process has a very significant contribution which can be seen from the fact that at dose values which are not high enough to lead to the formation of large iron clusters and yet high enough to surpass the limits of solid solubility, the contribution of iron monomers (non-associations) does appear in the CEM spectra. The Cracow group also studied ^{57}Fe implantation effects in silicon



(Sawicka and Sawicki 1977) and germanium (Sawicki and Sawicka 1977) over a dose range between 5×10^{14} and 5×10^{16} ions/cm². It has been shown that in Fe-Si, ion implantation leads to a broad doublet near the zero velocity channel indicating a distribution of hyperfine interaction which has a non-magnetic nature. The isomer shift and quadrupole splitting values corresponding to this doublet compare favourably with the parameters observed in the case of alloys formed by the coevaporation technique (Massenet and Daver 1976), thus establishing the rapid quenching nature of the implantation process. The appearance of this doublet can be attributed to the formation of iron dimers which occupy interstitial sites in the tetrahedral network and stabilize the amorphous surrounding, avoiding further clustering. The implantation studies on germanium (Sawicki and Sawicka 1977) also exhibit a number of interesting features regarding the relaxation in the implanted tetrahedral lattices, but the details of these studies will not be discussed here.

Dorik *et al* (1984) recently studied the oxidation properties of iron implanted with nitrogen ions by using the CEMS technique. In these experiments 80 keV N₂⁺ ions were implanted on iron foils at a dose of 2×10^{16} ions/cm² and a number of such samples in the as-implanted form or subsequent to a vacuum annealing treatment were subjected to oxidation treatment in air at the temperature range of 300°C to 500°C for 4 min in each case. The CEMS as well as conventional gravimetric measurements performed on these samples revealed that the as-implanted samples exhibit an enhanced oxidation rate as compared to the virgin iron foils. If one compares the spectra of figures 4 and 5a which correspond to the unimplanted and implanted samples oxidized at 300°C for 4 min respectively, it is clear that the oxide components (Fe₃O₄) and (Fe₂O₃) are



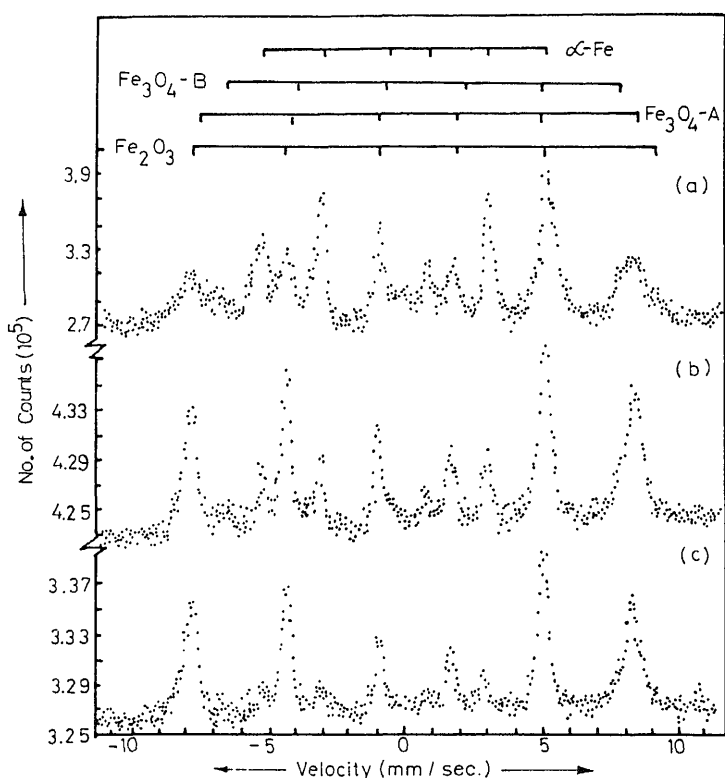


Figure 5. Room temperature CEM spectra of N_2^+ implanted iron foil heated in air at (a) 300°C, (b) 400°C (c) 500°C for 4 min each.

dominant in the implanted case when compared with the unimplanted sample. In fact, the ratio of the oxygen co-ordinated Fe to α -Fe has a value of 3.6 in the implanted case as against 0.96 in the unimplanted sample. These differences in the oxidation rate are also reflected in the gravimetric measurements given in figure 6. When the implanted foil which is annealed in a vacuum of 10^{-6} torr at 300°C for 30 min is oxidised, it shows a reduction in the oxidation rate even as compared to the rate exhibited by the virgin foil. This can be clearly seen by comparing the CEM spectra of figures 4 and 7a. The spectrum of figure 7a shows no detectable amount of oxide fractions indicating that the ion-implanted and vacuum-annealed foils show a significant improvement in the oxidation resistance of the virgin iron foils. This observation is confirmed by the gravimetric measurements given in figure 6. Figures 5 and 7 also show that at the oxidation temperature of 500°C both the implanted as well as the implanted and annealed foils exhibit considerable oxidation. It has been argued that ion implantation in iron produces defects and compressive stresses in the surface layers. Whereas the former effect enhances the oxidation rate due to defect-assisted diffusion, the latter effect tends to inhibit it, the overall effect in the implanted sample being a reduction in the oxidation resistance. The vacuum heat treatment (carried out at a temperature above the vacancy annealing temperature for α -iron of 140°C but below its recovery temperature of

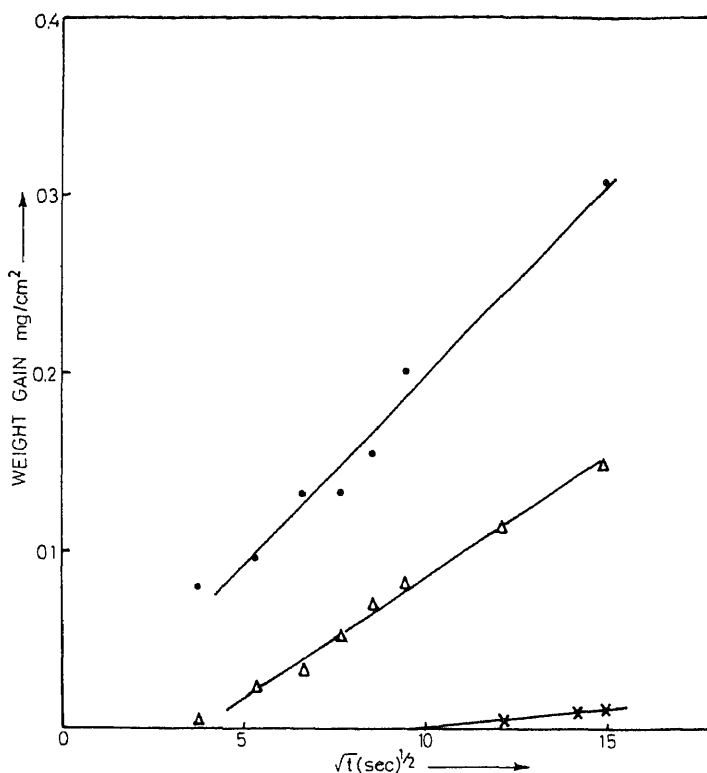


Figure 6. Results of gravimetric analysis for the unimplanted (Δ), N_2^+ implanted (.), N_2^+ implanted and annealed ($\times$) iron foils heat treated in air at 300°C .

migration of the implanted nitrogen atoms towards the grain boundaries and dislocation pipes resulting in the short circuit paths for oxygen indiffusion getting blocked. This can lead to the observed oxidation inhibition.

The examples discussed above show that the CEMS technique has a tremendous potential in investigating the properties of ion-implanted metals and alloys containing a suitable Mössbauer accessible element such as Fe. Very recently it has also been demonstrated that the CEMS technique is equally powerful in studying the physics of ion beam-induced interface reactions, which have been a subject of considerable interest in recent years. In what follows, we briefly review some of this work.

3. Ion beam mixing: CEMS studies

The first experiments on the use of the CEMS technique to study ion beam-induced interface mixing and subsequent reactions were carried out very recently by the Poona University group (Godbole *et al* 1984a, b, 1985; Ogale *et al* 1985a, b; Patankar *et al* 1985). The ion beam-induced interface reactions in the single interface Fe-Al (Godbole *et al* 1984a, b, 1985; Ogale *et al* 1985), Fe-Si (Ogale *et al* 1985a) and Fe-Ge (Patanekar *et al*

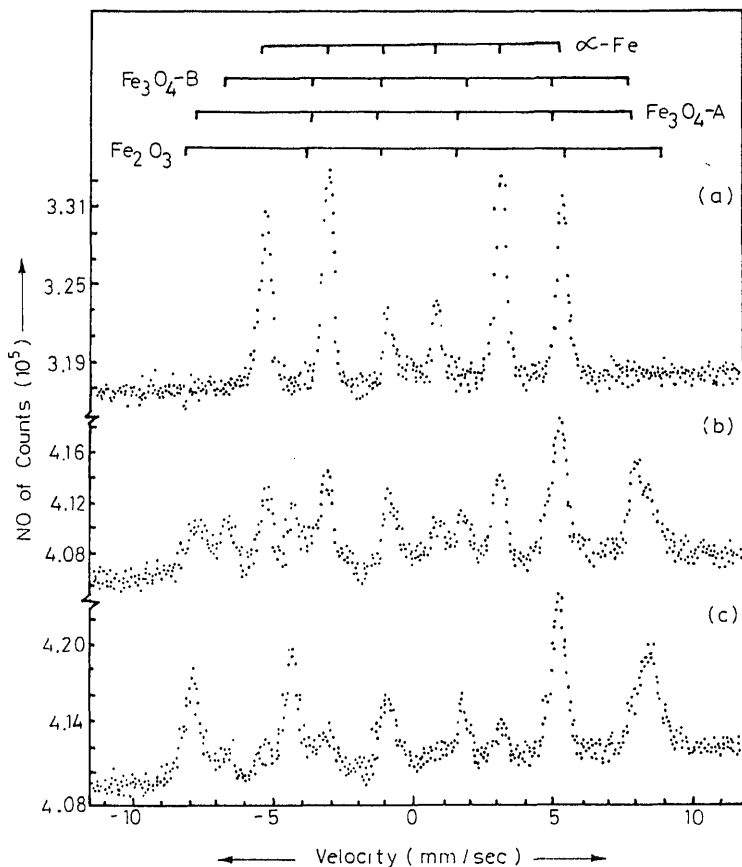


Figure 7. Room temperature CEM spectra of N_2^+ implanted and vacuum annealed (300°C for 30 min) iron foils heated in air at (a) 300°C , (b) 400°C , (c) 500°C for 4 min each.

electron Mössbauer spectroscopy; and interesting new information regarding the bombardment-induced interface phenomena has been brought out. In all these studies, an iron film (thickness $\sim 300 \text{ \AA}$) was deposited onto the aluminium, silicon and germanium substrates conditioned by appropriate thermal and chemical treatments. Since ion beam mixing occurs at the interface and grows across it, a novel method of sample preparation was adopted to obtain the Mössbauer information predominantly from the interface region. For this purpose an $\sim 50 \text{ \AA}$ film of ^{57}Fe Mössbauer isotope enriched to 95-45% was deposited on the substrates of Al, Si and Ge, followed by a deposition of an $\sim 250 \text{ \AA}$ thick film of natural iron which contains only 2.2% of the ^{57}Fe isotope (figure 8). Since the Mössbauer signal emanates only from the ^{57}Fe nuclei, using this sample preparation procedure an interface sensitive CEM spectroscopic study could be carried out and the early interface reactions in the ion beam mixed region could be really understood.

The first system in which the ion beam mixing process was characterised by the surface sensitive CEMS technique was Fe-Al. This system was chosen for the following

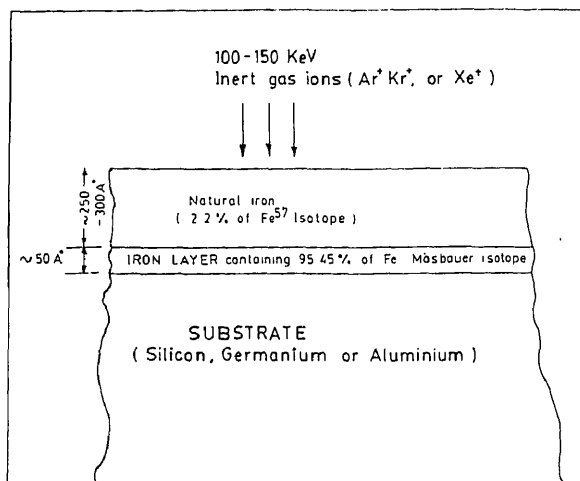


Figure 8. Sample for interface sensitive CEM spectroscopic studies.

of one of the components of this system; (ii) the equilibrium solid solubility of Fe in Al is extremely low i.e. only ~ 0.005 at. % even upto 450°C , with the result that the conventional thermal treatment does not lead to any substantial interface reaction in this system; which enables one to clearly identify the characteristic differences between the ion beam induced and pure thermal reactions at the interface of two elemental solids; (iii) the phase diagram of the Fe-Al system is extensively investigated and it shows the existence of a large number of phases such as $\text{Fe}_4\text{Al}_{13}$, FeAl , Fe_2Al_5 , Fe_3Al , FeAl_6 etc., which is a favourable situation in so far as the occurrence of mixing at the interface is concerned, according to the empirical rule established earlier; (iv) Al being a low-Z material, it does not produce a high photoelectron background and thus the CEM spectra are expected to be of good quality in this system; and (v) Al being non-magnetic, it does not create any complications in elucidating the magnetic hyperfine interactions at the ^{57}Fe nuclei. Many Fe-Al samples, prepared following the procedure mentioned above, were implanted with 100 keV Ar^+ ions at a dose range between 1×10^{16} and 3×10^{16} ions/cm² to achieve the interface mixing. The fact that the interface mixing has occurred was confirmed by Rutherford backscattering measurements (figure 9), which also brought out the average composition of the mixed zone to be $\text{Fe}_{5.5}\text{Al}_{4.5}$. The as-deposited as well as ion beam mixed samples were annealed at a background vacuum of 10^{-6} torr at various temperatures upto a maximum of 600°C and the transformations in the CEM spectra were monitored. All the spectra were computer-analysed following the conventional Mössbauer fitting procedure along with that for obtaining the distribution of magnetic hyperfine field (Window 1971).

The CEM spectra of the as-deposited sample and the corresponding hyperfine field distribution are shown in figures 10a and 10e respectively. In addition to the h.f. field of 330 kOe corresponding to $\alpha\text{-Fe}$, the h.f. distribution also shows another dominant magnetic interaction corresponding to a field value of 240 kOe, and an intense low field component which could indeed be due to the quadrupole and not the magnetic

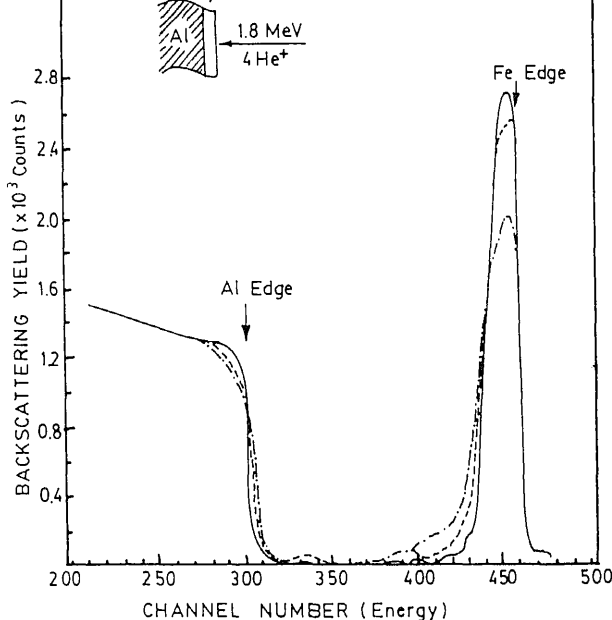


Figure 9. Rutherford backscattering spectra (RBS) of the as-deposited and ion beam mixed composites. The continuous line corresponds to the as-deposited sample, the dashed line corresponds to the sample bombarded with 100 keV Ar^+ ions at a dose of 1×10^{16} ions/ cm^2 and the dash-dot line corresponds to the sample bombarded with 100 keV Ar^+ ions at a dose of 3×10^{16} ions/ cm^2 .

happen due to the deposition-induced reaction. The apparent low field magnetic component could indeed be fitted with a quadrupole doublet contribution having the h.f. interaction parameters of isomer shift $\delta = 0.33$ mm/sec and the quadrupole splitting $\Delta = 1.018$ mm/sec. The appearance of this doublet was attributed to the presence of ^{57}Fe atoms in the $\gamma\text{-Al}_2\text{O}_3$ skin on the surface of aluminium (Preston 1972) (this natural oxide of Al is always present on the aluminium surface in the form of an ultrathin film). When bombarded with Ar^+ ions the CEM spectrum shows a drastic change [see figure 10b, f for the field distribution ($P(H)$ curve)]. Figure 10f shows a considerable reduction of the peak at 330 kOe corresponding to $\alpha\text{-Fe}$ and emergence of low field components at field values of 100 kOe, 192 kOe and 252 kOe. It may be hypothesized that the local atomic coordination in the ion beam mixed region fluctuates randomly between the aluminium-like (*i.e.* f.c.c.) and iron-like (*i.e.* b.c.c.) environments. It is possible to find a certain specific number of aluminium near-neighbours in the b.c.c. like (8 neighbours, Fe-b.c.c.) and f.c.c. like (12 neighbours, Al-f.c.c.) atomic environment by using the binomial distribution. From such a distribution one can deduce the distribution of internal field by assuming a lowering of the value of this field at ^{57}Fe nucleus per aluminium neighbour to be ~ 26 kOe (Oswald *et al* 1978). By this method one may expect to obtain a distribution which resembles at least certain portions of the observed $P(H)$ distribution curve. This is indeed found to be true as seen

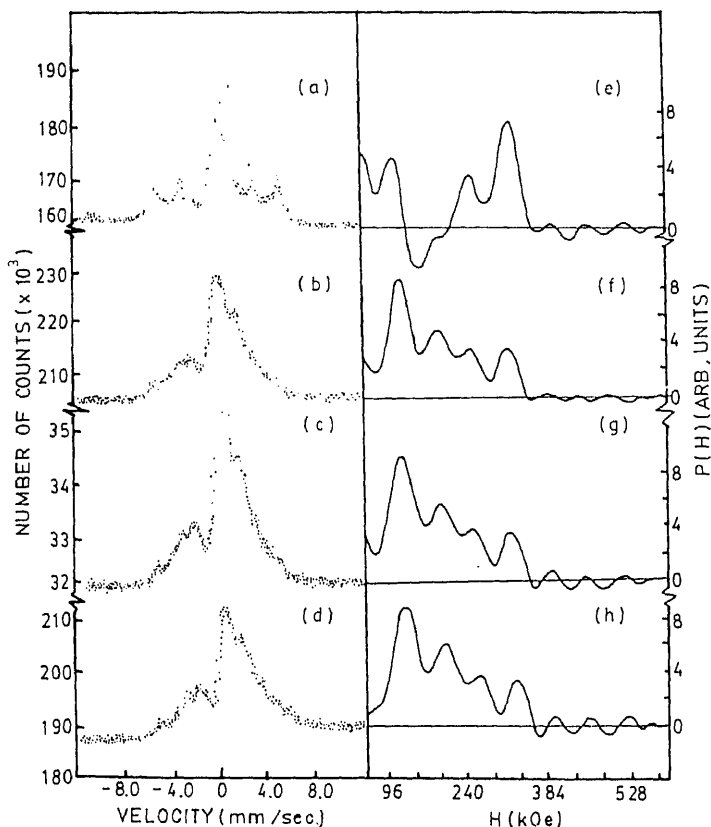


Figure 10. Room temperature CEM spectra of (a) as-deposited and (b) ion beam mixed Fe-Al composite. The spectra (c) and (d) represent ion beam mixed samples annealed at 300°C and 400°C respectively for 20 min each. The curves in (e), (f), (g) and (h) are the hyperfine field distribution plots corresponding to the spectra in (a), (b), (c) and (d) respectively.

from figure 11. The peaks at 192 and 252 kOe can thus be attributed to the fluctuations of atomic coordination between 8 and 12 neighbour environments. The peak at 100 kOe (lower field) can possibly be attributed to the dilute magnetic alloy of Fe in aluminium on the aluminium side of the interface.

When the ion beam mixed sample is annealed at 300°C and 400°C for 20 min in each case, the corresponding CEM spectra (figures 10c,d and the field distributions, figures 10g, h) do not show any significant changes from the characteristics exhibited by the ion beam mixed sample. When annealed at 500°C for 20 min, however, the spectral features show a drastic change, and the standard computer fitting procedure reveals the presence of α -Fe and Fe_3Al phases (Gonser and Ron 1980) (figure 11) in the sample. This sample when further annealed at 600°C shows another drastic change in the CEM spectrum, which now indicates the presence of a small contribution of α -Fe and a large contribution of a central doublet component. The h.f. interaction parameters corresponding to the doublet match reasonably well with the parameters correspond-

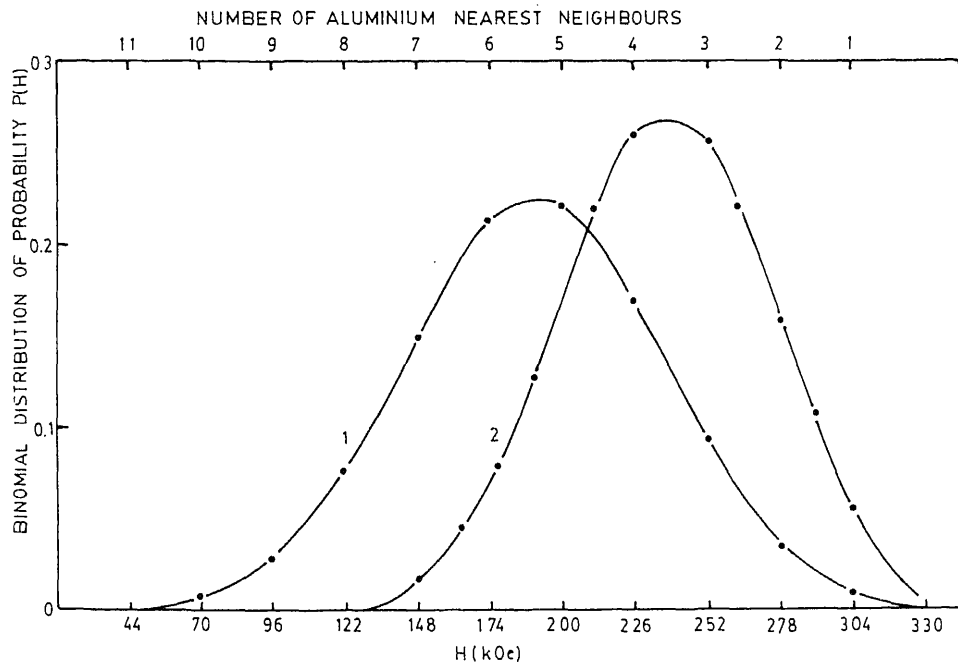


Figure 11. Probability distribution function $P(n)$ for n Al to be near neighbours to Fe in a random alloy $\text{Fe}_{55}\text{Al}_{45}$ using the standard binomial distribution and the corresponding hyperfine field distribution $P(H)$ for local atomic coordination 12 (curve 1) and 8 (curve 2).

spectra continued to show the presence of α -Fe with an increase in the intensity of this spectral component and a gradual reduction of the central doublet corresponding to ^{57}Fe in Al_2O_3 skin, which could be due to the out-diffusion of iron from the oxide. No Fe_3Al phase was observed in the as-deposited sample annealed at 500°C , which showed the presence of only α -Fe. This clearly brings out the difference between the characteristics of the thermally-induced interface reactions in the as-deposited and ion beam mixed samples.

The Poona group has also studied the dose dependence of ion beam mixing at the Fe-Al interface (Ogale *et al* 1985b). For this purpose, non-interface sensitive studies were carried out in which the samples were prepared by depositing iron overlayer (containing $\sim 30\%$ of the enriched ^{57}Fe isotope uniformly distributed over the film region) onto the aluminium substrates. Such non-interface sensitive studies were undertaken primarily to understand the nature of the change in the beam mixing process when the ion dose is raised from a low value of less than $\sim 5 \times 10^{14}$ ions/ cm^2 at which individual cascade effects dominate, to the high doses at which the cascade overlap effects start playing an important role. The non-interface sensitive method was used in the place of the interface sensitive one in these studies because the interface sensitive technique defines a fixed length scale (of ~ 50 Å) at the interface, which is not compatible to the growth of the mixed region as a function of the increase of the ion

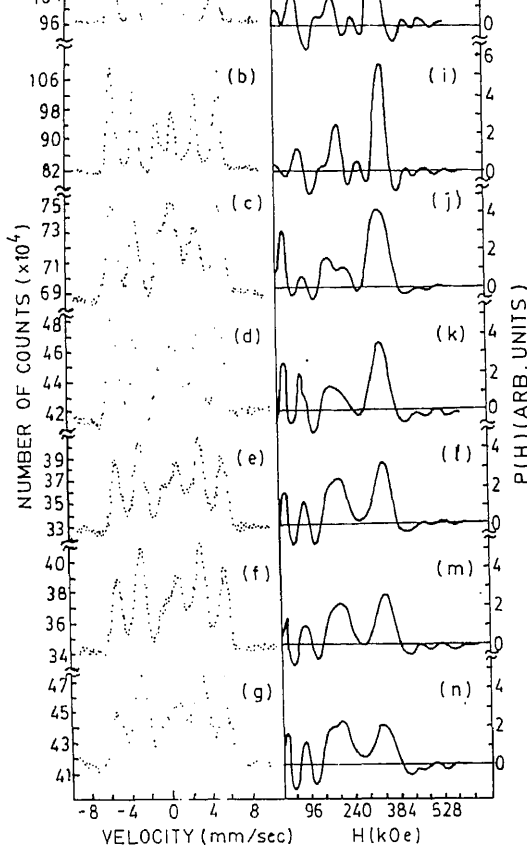
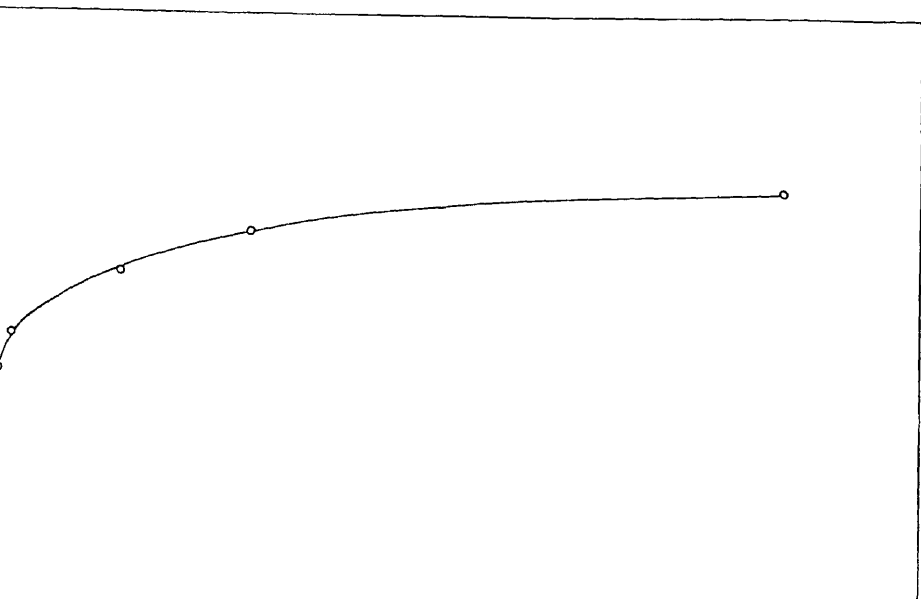


Figure 12. Room temperature CEM spectra of (a) as deposited Fe-Al composite and ion beam mixed Fe-Al composite with a dose of (b) 1×10^{14} ions/cm² (c) 5×10^{14} ions/cm² (d) 1×10^{15} ions/cm², (e) 5×10^{15} ions/cm², (f) 1×10^{16} ions/cm², (g) 3×10^{16} ions/cm². The corresponding hyperfine field distribution curves are represented with continuous curves.

CEM spectra of the composites implanted with Ar⁺ ions at various values of ion dose ranging between 10^{14} ions/cm² and 3×10^{16} ions/cm² are shown. The distributions of internal magnetic field have also been given for all the spectra. The distribution corresponding to the as-deposited sample exhibits a peak at 330 kOe (which corresponds to α -Fe) and other small variations which can partly be attributed to the use of Fourier series in the decomposition procedure upon ion beam mixing. With increasing implantation dose the peak at 330 kOe shows a systematic decrease in intensity with emergence of peaks corresponding to lower values of hyperfine fields. Also the line-widths of the Mössbauer spectral components show an increase with implantation dose, indicating the presence of disorder in the mixed zone. The emergence of peaks corresponding to lower field values is due to formation of an

surface alloy in which the ^{57}Fe nuclei find one or more of aluminium neighbours which contribute to the decrease of hyperfine field. When integrated over the entire range of lower field values distinguishable from the peak at 330 kOe, the total low field contribution shows a gradual increase with ion dose (figure 13). It may be noted, however, that the increase is almost linear upto a dose of 10^{15} ions/cm² beyond which the nature of the curve and hence possibly the mixing process, shows a deviation (Poate *et al* 1981). It is interesting to note that the dose value of 10^{15} ions/cm² is typically the dose at which the cascade overlap effects may be expected to dominate the mixing process. It is possible to separately fit the low field components of the Mössbauer spectra by the standard Mössbauer fitting procedures and to identify the nature of the microstructure. This exercise is presently being carried out.

In addition to the Fe-Al system, the Fe-Si (Ogale *et al* 1985a) and Fe-Ge (Patankar *et al* 1985) systems have also been investigated by the Poona group. The Fe-Si system exhibits features similar to those observed in the Fe-Al system, though at a relatively higher temperature. On the other hand, the Fe-Ge system exhibits a behaviour which is distinctly different as compared to the Fe-Al and Fe-Si systems. In the Fe-Ge case the transformations are more gradual and the Fe-enrichment process begins at a temperature as low as 350°C. The similarities and differences in the behaviour exhibited by the three systems correspond reasonably well to the atomic and solid state parameters of the elements involved.



ion beam mixing process carried out by employing the CEMS technique. Using the same technique the Poona group has also investigated the applied nature on the ion beam mixed state of Fe-Al alloy, in which the electrochemical corrosive properties of these alloys have been studied (Kanetkar *et al* 1985). In these experiments the as-deposited as well as ion beam mixed Fe-Al samples prepared for interface sensitive CEMS measurements were subjected to electrochemical corrosion by employing the three sweep potentiokinetic polarization technique. The use of the three sweep technique, suggested by Ashworth *et al* (1976) for electrochemical studies of corrosive properties of implanted solids was made to eliminate any possible interference of the air-formed oxide film in the evaluation of the corrosive properties of the ion beam mixed region. We carried out potentiokinetic polarization measurements at two sweep rates. A sweep rate of 1.33 mV/sec corresponding to a quasi-steady state condition was used to simulate the situation of practical importance, while a higher sweep rate of 10 mV/sec was used to understand the dynamical features of the corrosive activity. A higher sweep rate is also useful to obtain a clear active-to-passive transition in cases where such a transition cannot be seen, in view of the thinness of the films as compared to the length scale of corrosive activity. The electrochemical corrosion was measured at room temperature in an acetic acid/sodium hydroxide buffer solution having a pH of 6.95.

From figure 14, it is observed that the Fe foil shows active-to-passive transition for

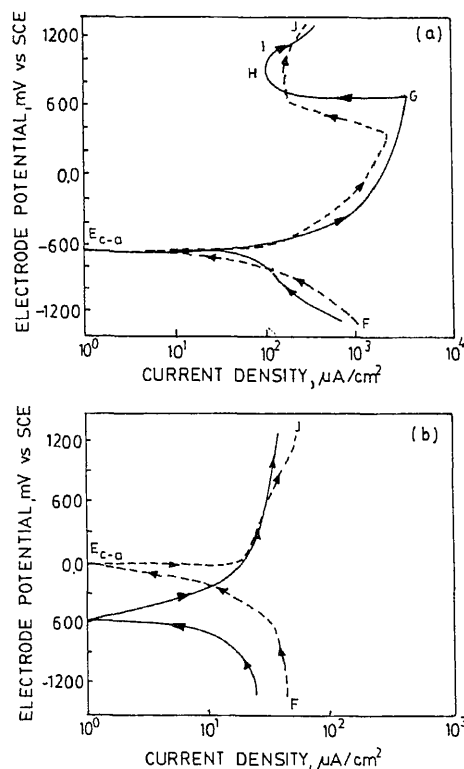
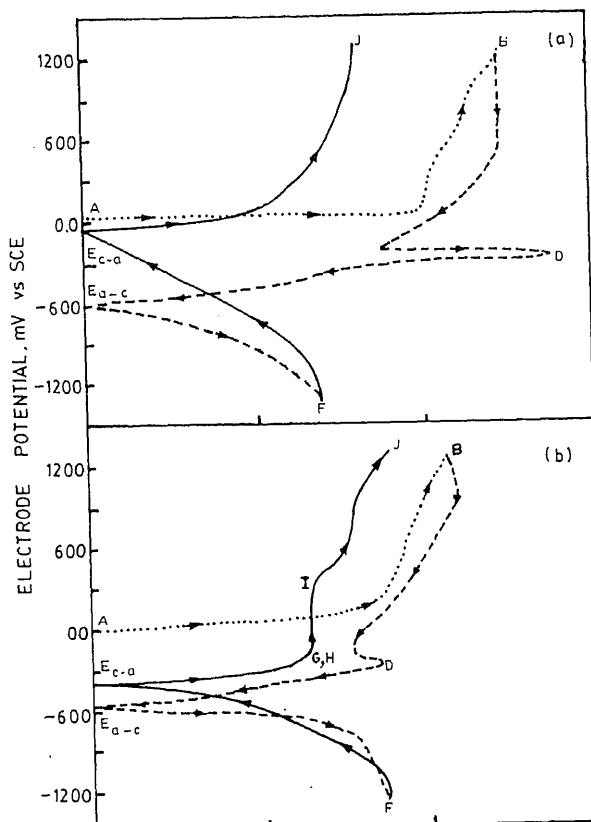


Figure 14. Second positive going sweep in the three sweep potentiokinetic polarisation curves for (a) pure iron foil (b) pure aluminium foil. The continuous line and dashed curves

both the sweep rates. The values of critical current density and pitting potential are lower in the higher sweep rate as compared to the lower sweep rate. In aluminium, no active-to-passive transition is observed at either values of the sweep rate (figure 14b), because subsequent to an initial dissolution, the passivation ensues almost immediately due to the formation of an aluminium oxide coating in the aqueous medium.

When the as-deposited sample was subjected to electrochemical corrosion, the iron layers deposited on the aluminium substrates dissolved for both the sweep rates employed. On the other hand, the ion beam mixed Fe-Al sample exhibited distinctly different features as compared to as-deposited Fe-Al sample (figures 15 and 16). An examination of figures 15a, b clearly shows that the dissolution of iron is considerably higher in the as-deposited sample as compared to the ion beam mixed sample. This is indicated by the current density corresponding to the point D on the curve of the first negative going sweep. It is also observed that the as-deposited sample does not show any active-passive transition and indicates a dissolution similar to that of pure aluminium. At faster sweep rate (figure 16) the active-to-passive transition and the corrosion inhibition in ion beam mixed sample are seen more clearly.



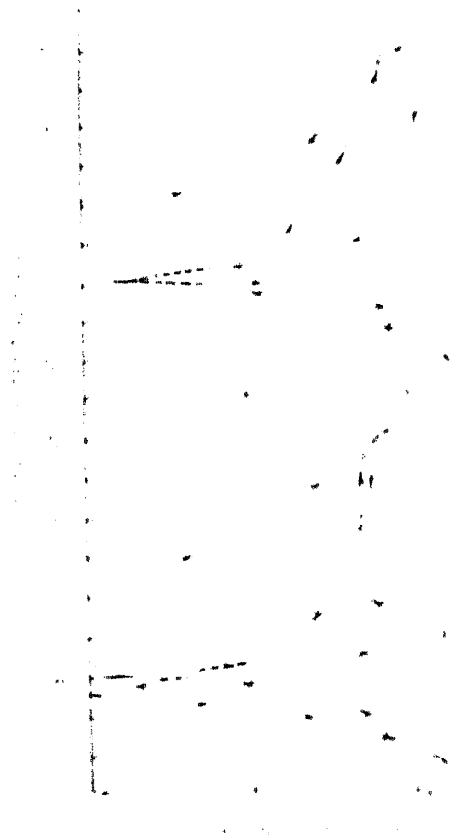


Figure 16. Three sweep potentiokinetic polarisation curves for: (a) deposited sample, (b) ion beam mixed Fe-Al composite. The dotted curve corresponds to first positive sweep, dashed curve corresponds to the first negative going sweep and the solid curve corresponds to second positive going sweep at the scan rate of 10 mV/sec.

In order to understand the physics of the corrosive properties exhibited by the ion beam mixed sample we characterised this sample before and after the corrosive attack by using the xms technique. The xms spectrum of the ion beam mixed sample (figure 17b) is significantly different as compared to that of the deposited sample (figure 17a) and the corresponding magnetic field distribution (figure 17c) shows peaks at 100, 192, 252 and 330 kOe. On comparing figure 17d with figure 17c it is clearly seen that the peak at 330 kOe which corresponds to α -Fe is considerably reduced and low field components are increased upon ion bombardment. This means that significant atomic mixing has occurred at the interface. The average composition of the mixed layers obtained by xms technique turns out to be $\text{Fe}_{47}\text{Al}_{53}$. The details of the xms spectrum and the corresponding field distribution have already been discussed in this paper. In the present context it may only be mentioned that the ion beam mixed interface is a disordered alloy with significant fluctuations in local alloy structure.

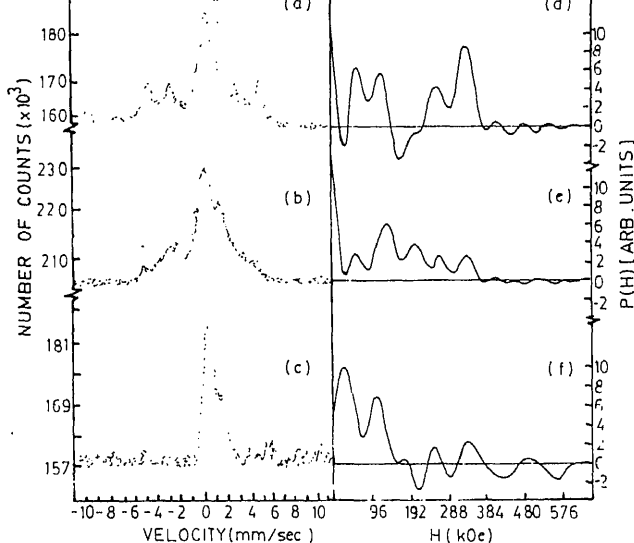


Figure 17. Room temperature CEM spectra of Fe-Al composite: (a) as-deposited (b) ion beam mixed and (c) ion beam mixed composite subjected to aqueous corrosion. Hyperfine field distributions corresponding to the spectra in (a), (b) and (c) are shown in (d), (e) and (f) respectively.

absence of Fe, we recorded the CEM spectrum of the as-deposited sample after electrochemical corrosion. No resonant absorption could be seen showing a complete dissolution of the iron film. On the other hand, the ion beam mixed sample led to CEM spectrum as shown in figure 17c. When decomposed, this spectrum gives magnetic hyperfine field distribution as given in figure 17f. It can be readily seen that the peaks at 192 and 252 kOe in the field distribution corresponding to the ion beam mixed sample are decreased substantially upon corrosion while the peak at ~ 100 kOe is shifted to a lower field value of ~ 90 kOe. It is also observed that the peak at 330 kOe is decreased to a certain extent. In addition to these changes in the magnetic components we could fit the total spectrum of figure 17c with two quadrupole-split doublets. One of the doublets has an isomer shift of 0.40 mm/sec and a quadrupole splitting of 0.63 mm/sec, while the other doublet has an isomer shift of 0.89 mm/sec, and a quadrupole splitting of 1.27 mm/sec. The hyperfine parameters of the latter doublet match reasonably well with those of FeO (Terrell and Spijkerman 1968; O'Grady 1980; Eldridge *et al* 1982) (I. S. = 0.91 mm/sec, Q. S. = 0.80 mm/sec) except for a higher value of the quadrupole splitting which may be attributed to the thinness of the ion beam mixed film and to the damage imparted to the interface structure due to the ion bombardment. The hyperfine parameters of the other doublet can be favourably compared to those of hydrated non-magnetic oxides of Fe (Terrell and Spijkerman 1968; O'Grady 1980; Eldridge *et al* 1982) such as, γ -FeOOH (I. S. = 0.38 mm/sec, Q. S. = 0.59 mm/sec), β -FeOOH, (I. S. = 0.37 mm/sec, Q. S. = 0.71 mm/sec and also α -Fe₂O₃ clusters (Kundig *et al* 1966) (I. S. = 0.31 mm/sec and Q. S. = 0.98 mm/sec).

obtained in the ion beam mixed sample can be attributed to the growth of the above mentioned phases on the sample surface. The small difference between the hyperfine parameters of the passive film on the ion beam mixed surface and the above mentioned phases may be due to the presence of aluminium in the matrix. This interesting point which concerns with the internal compound states of an alloy needs further investigation. We are presently investigating the influence of ion dose, which leads to the growth of the ion beam mixed region as well as changes in its microstructural properties on the corrosive behaviour of ion bombarded Fe-Al composites. Further work employing the CEMS method to study the oxidation properties of ion beam mixed phases and the formation of amorphous oxides by ion beam mixing technique is also in progress in our laboratory.

4. Conclusions

In view of the important role played by surfaces and interfaces in a variety of physical and chemical processes, there is a growing interest in both the modification of surfaces to the required specifications and characterization of surfaces at the atomic level. So far as surface modification is concerned the newer techniques such as ion implantation, ion beam mixing, electron and laser beam treatment offer many advantages and novel approaches. In the characterization of radiation-processed surface layers, in addition to the conventional techniques, the technique of CEMS also proves to be extremely useful since it can bring out valuable information concerning atomistic aspects of irradiated materials.

Acknowledgements

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Influence of charge on the stability of 5'-cytidine monophosphate in solution

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Keywords. 5'-Cytidine monophosphate (5'-CMP); Lanthanides; metal-ligand interactions; stability constant; charge effects.

1. Introduction

The nucleotides constitute the back bone structure of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The importance of metal ions in biological processes like transcription, replication and translation reactions are very well established. Therefore, the attention the metal-nucleotide interactions have received, especially during the last decade is not surprising (Marzilli *et al* 1980; Hodgson 1977; Gillert and Ban 1977; Martin and Mariam 1979; Wilson *et al* 1982; Orenburg *et al* 1980; Scheller *et al* 1981). Among the nucleotides, mostly the nucleotide triphosphates have been studied (Taqui Khan and Rabindra Reddy 1973a, b, 1975, 1976; Taqui Khan and Martell 1967; Wallas 1958). However, very little is known on metal-mononucleotide interactions and that too with bivalent metal ions. The data with metals of higher oxidation states are not available in the literature. Therefore, it was considered important to investigate the interaction of 5'-cytidine monophosphate with various metal ions. Earlier we have studied the interaction of 5'-cytidine monophosphate with transition and alkaline earth metal ions along with other related systems (Rabindra Reddy *et al* 1985). In the present manuscript, we have extended our investigations to the trivalent lanthanides to study the influence of charge on the stability of the mononucleotides.

2. Experimental

5'-Cytidine monophosphate was obtained from the Sigma Chemical Company, U.S.A. All rare earth oxides were of Johnson Mathey's spectral grade and a stock solution was prepared by dissolving a known weight of the oxide in pure nitric acid. The lighter lanthanides were standardized with the disodium salt of EDTA (Schwarzenbach 1957). The heavier lanthanides were estimated gravimetrically as oxides (Kolthoft and Elving 1963). Carbonate-free sodium hydroxide was prepared and was standardized by titration with potassium acid phthalate.

The experimental method employed consisted of the potentiometric titration of the

ion being investigated. All titrations with metal ions were carried out in a 1:1 ratio of metal ions and the ligand at $35 \pm 0.1^\circ\text{C}$. However, the experimental details can be found in one of our recent papers (Rabindra Reddy *et al* 1984).

3. Calculations

3.1 Acid dissociation constants

The acid dissociation constants K_a and K_{2a} of the ligand were calculated with the aid of the graphical method (Martell and Calvin 1952). In the graphical method a relationship between K_a and K_{2a} can be expressed in terms of known quantities by (1):

$$B = (K_{2a} \cdot B/A) - (1/K_a) \quad (1)$$

where

$$A = \frac{\{(a-1)T_L - [H^+]\}}{\{(2-a)T_L/[H^+]\} - 1} \quad \text{and} \quad B = \frac{\{(a-1)T_L + [H^+]\}}{\{[H^+](aT_L + [H^+])\}}$$

A plot of B versus B/A gives a straight line with slope equal to K_{2a} and intercept equal to $1/K_a$.

3.2 Stability constants

In order to calculate the stability constants of the binary complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III) and Er(III) with 5'-cytidine monophosphate in a 1:1 ratio, the following equations were used (excluding the charges).



together with related equilibria,



$$K_{ML}^M = \frac{[M][L]}{[ML]} \quad (4)$$

$$[L] = \frac{\{(2-m)T_L - [H^+] + [OH^-]\}}{(2[H^+]^2/K_{1a}K_{2a}) + ([H^+]/K_{2a})}$$

$$[M] = [L] \{([H^+]^2/K_{1a}K_{2a}) + ([H^+]/K_{2a}) + 1\}$$

$$[ML] = T_L - [M]$$

where,

$[L]$ = concentration of free ligand;

$[M]$ = concentration of free metal ion;

$[ML]$ = concentration of complex formed;

m = moles of base added per mole of the metal ion;

a = moles of base added per mole of ligand;

T_L = total concentration of the ligand species present in solution.

4. Results

The ligand titration curves of 5'-cytidine monophosphate given in figure 1 (X) shows an inflection at $a = 2$ indicating the simultaneous dissociation of two protons. The acid dissociation constants were calculated graphically, as described in the calculation section and were presented in table 1. The titration curve of Dy(III)-5'-cytidine monophosphate in a 1:1 ratio is given in figure 1 (Y). Invariably a precipitate appeared before the inflection point could be reached (at $a \approx 1.8$) for all the systems studied. However, it was assumed that a normal 1:1 complex, K_1 , is formed between the buffer regions $a = 0$ and $a = 2$ and the stability constants were calculated with the help of (4) by taking experimental points far below the precipitation regions. The assumption of a simultaneous formation of a protonated and normal complex gave negative results. The constants thus calculated are presented in table 1.

5. Discussion

The closeness in the pK_a value of 5'-cytidine monophosphate with those of cytosine (4.20) (Taqui Khan and Krishnamurthy 1974) and cytidine (4.19) (Rabindra Reddy and Malleswara Rao 1985) suggests that the dissociation of the first proton is from the same site i.e., N_3-H . The second ionization of 5'-cytidine monophosphate is from the phosphate moiety, whose value of 6.56 is consistent with the values reported for similar systems. The dissociation steps of the 5'-cytidine monophosphate are given in figure 2.

The stability constants of 5'-cytidine monophosphate with rare earths decrease in the

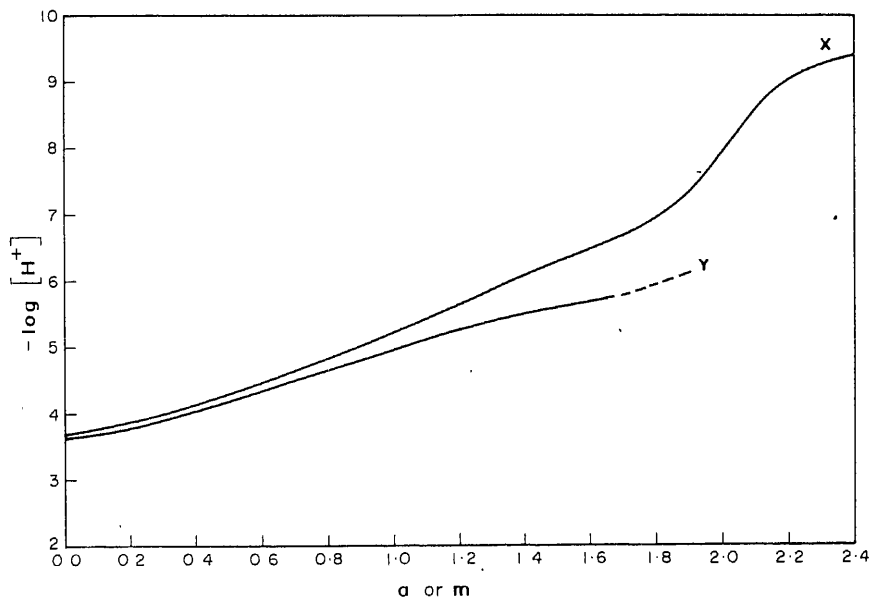


Figure 1. Interaction of Dy(III) with 5'-cytidine monophosphate in a 1:1 ratio and 0.10 M 5'-cytidine monophosphate at 25°C. $K_1 = 10^{4.2}$, $K_2 = 10^{6.6}$, $K_3 = 10^{10.5}$, $K_4 = 10^{10.5}$.

Table 1. Stability constants associated with interaction of metal with 5'-cytidine monophosphate in a 1:1 ratio.

Metal	Metal 5'-CMP $\log K_1$
La(III)	3.73 ± 0.02
Pr(III)	3.84 ± 0.02
Nd(III)	4.01 ± 0.03
Sm(III)	4.11 ± 0.03
Gd(III)	4.20 ± 0.03
Dy(III)	4.21 ± 0.04
Er(III)	4.35 ± 0.04

$\mu = 0.10 \text{ M (KNO}_3\text{)}$; temperature
 $= 35^\circ\text{C}$; $pK_a = 4.40$, $pK_{2a} = 6.56$.

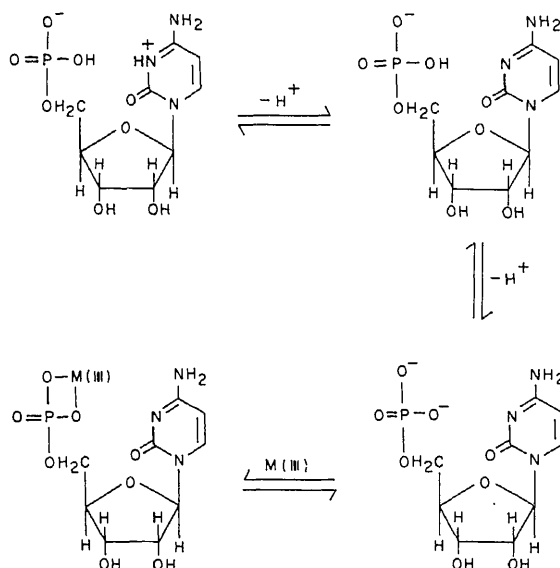


Figure 2. Schematic representation of the dissociation and association steps of 5'-CMP, M(III) = trivalent metal ion.

order: Er(III) > Dr(III) > Gd(III) > Sm(III) > Nd(III) > Pr(III) > La(III). The stability constants are inversely proportional to their ionic radii, a trend that is observed for a variety of ligands with lanthanons. It is of interest here to compare the stability constants of trivalent lanthanons with those of bivalent transition metal ions. 5'-cytidine monophosphate forms more stable complexes with the former as compared to the latter (Rabindra Reddy *et al* 1985). This may be explained on the basis of differences

approach of the ligands and larger electrostatic attraction resulting in the formation of stable complexes with the mononucleotide as compared to the less charged transition and alkaline earth metal ions. However, the magnitude of the stability data suggests that in the tri- and bivalent metal ions the nature of bonding may be similar. Based on this we propose a tentative structure for the lanthanide-5'-cytidine monophosphate interactions (figure 2).

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Lanthanide perchlorate complexes of quinoline-1-oxide and isoquinoline-2-oxide

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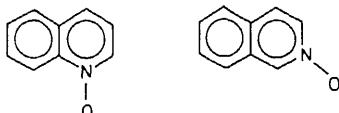
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Abstract. Complexes of lanthanide perchlorates with quinoline-1-oxide and isoquinoline-2-oxide, have been isolated for the first time and characterised by analysis, conductance, and IR, NMR and electronic spectral studies. The complexes of quinoline-1-oxide have the composition $\text{Ln}(\text{QNO})_8(\text{ClO}_4)_3$ where $\text{Ln} = \text{La}, \text{Pr}$ or Nd and $\text{Ln}(\text{QNO})_7(\text{ClO}_4)_3$ where $\text{Ln} = \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}$ or Yb . The isoquinoline-2-oxide complexes analyse for the formula $\text{Ln}(\text{IsoQNO})_7(\text{ClO}_4)_3$ where $\text{Ln} = \text{La-Yb}$.

Keywords. Lanthanide perchlorates; quinoline-1-oxide; isoquinoline-2-oxide; proton NMR; electronic spectra; IR spectra; electrolytic conductance.

1. Introduction

Quinoline-1-oxide (QNO) and isoquinoline-2-oxide (isoQNO) are analogues of 2,3- and 3,4- disubstituted pyridine-1-oxide (PyNO) respectively. In general, QNO and isoQNO do not introduce severe steric hindrance during the formation of cationic complexes with transition metal ions (Karayannis *et al* 1973), and complexes of QNO and isoQNO are of the formulae similar to those obtained for the corresponding PyNO complexes. But in some of the adducts, the difference in the steric influence of QNO and isoQNO is reflected in the stoichiometry of the respective adducts. For example while QNO forms a 1:1 adduct with $\text{M}(\text{AcAc})_2$ [$\text{M} = \text{Ni}, \text{Co}$, $\text{AcAc} = \text{acetyl acetate}$], isoQNO forms a 2:1 adduct with these chelates (Kluiber and Horrocks 1966). QNO complexes of lanthanide chlorides (Kingston *et al* 1969), of lanthanide iodides (Ramakrishnan and Soundararajan 1977) and of lanthanide hexathiocyanochromates(III) (Serebrinnikov *et al* 1969) and complexes of isoQNO with lanthanide iodides (Ramakrishnan 1977) have already been reported. In the complexes of QNO with lanthanide chlorides [$\text{Ln}(\text{QNO})_3\text{Cl}_3\text{H}_2\text{O}$ for $\text{Ln} = \text{Nd}, \text{Sm}$ and



$\text{Ln}(\text{QNO})_4\text{Cl}_3\text{H}_2\text{O}$ for $\text{Ln} = \text{Eu-Ho, Yb}$], the L:M increases with decreasing metal ion radius, violating the general trend in which L:M decreases with decreasing metal ion radius. The low L:M ratio is due to the coordination of the anions in these complexes. The stoichiometry of the $[\text{Ln}(\text{QNO})_x][\text{Cr}(\text{NCS})_6]$ (where $X = 6, 7$ and 8) indicates that the bulkiness of the QNO molecule may have little effect on the L:M ratio in these complexes, compared to the corresponding PyNO complexes $[(\text{Ln}(\text{PyNO})_8)][\text{Cr}(\text{NCS})_6]$ (Pavlenko *et al* 1971, 1973). IsoQNO yields complexes of the type $\text{Ln}(\text{isoQNO})_8\text{I}_3$ with lanthanide iodides (Ramakrishnan and Soundararajan 1977) except with Pr(III) iodide, where it appears as if the ligand does not impart severe steric hindrance to coordination at the coordination site. Thus even though both QNO and isoQNO have almost the same bulk, the position of the N-O group seems to have an influence on the stoichiometry of the complexes with these ligands. The low L:M ratio in the QNO complexes may also be due to the nature of the solvent used in the synthesis of these complexes.

In order to understand the difference in the coordinating nature of QNO and isoQNO, we have presently prepared the lanthanide perchlorate complexes of these ligands in the absence of coordinating solvents and where the perchlorate anion will be completely ionic and noncoordinate. The isolated complexes have been studied by analysis, conductance, IR, NMR and electronic spectra.

2. Experimental

2.1 Materials

Quinoline and isoquinoline were obtained from SD chemicals, India and Fluka, Germany respectively. Lanthanide oxides (99.9%) were obtained from Indian Rare Earths Ltd., Kerala. All the other chemicals were of reagent grade. The solvents were purified by standard methods.

2.2 Preparation of the ligands

Quinoline-1-oxide and isoquinoline-2-oxides were prepared (Ochiai 1953) by the N-oxidation of quinoline and isoquinoline respectively, purified and recrystallised from an ether-acetone mixture and an ethyl acetate solution, respectively. QNO: m.p. 57° (literature 58°); isoQNO: m.p. 104°C (literature 103°C).

2.3 Preparation of the hydrated lanthanide perchlorates

The hydrated lanthanide perchlorates were prepared by dissolving the corresponding oxides in 50% perchloric acid and evaporating the solution on a steam bath.

2.4 Preparation of lanthanide perchlorate complexes

To a hot solution of QNO or isoQNO (10 mM) in ethylacetate (30 ml), a solution of hydrated lanthanide perchlorate (1 mM) in ethyl acetate (5 ml) was added dropwise with stirring. Stirring in the hot condition was continued till the completion of the reaction. The precipitated complex was filtered, washed two to three times with hot

2.5 Analyses

The metal contents of the complexes were estimated by EDTA titrations using xylenol orange as indicator (Lyle and Rahman 1963). The perchlorate was estimated by gravimetric precipitation with nitron as described by Welcher (1947). The ligands QNO and isoQNO were estimated spectrophotometrically at 310 nm and 295 nm respectively using the calibration curve method (Willard *et al* 1965). The analytical data are presented in table 1.

2.6 Physical methods

The IR spectra of the complexes and the ligands in nujol mulls, in the region 400–4000 cm^{-1} , were recorded on Perkin-Elmer model-397 spectrophotometer. The principal IR bands and their tentative assignments are given in table 2.

Proton NMR spectra of the diamagnetic complexes and the ligands were recorded on a

Table 1a. Analytical and molar conductance data for QNO complexes.

Complex	% Metal		% Ligand		% ClO ₄ ⁻		λ _m [*] (ohm ⁻¹ cm ² mole ⁻¹)
	Found	Calculated	Found	Calculated	Found	Calculated	
<i>Quinoline-1-oxide complexes</i>							
[La(QNO) ₈](ClO ₄) ₃	8.64	8.69	73.90	72.63	18.47	18.68	348.2
[Pr(QNO) ₈](ClO ₄) ₃	8.96	8.81	73.81	72.53	—	—	350.8
[Nd(QNO) ₈](ClO ₄) ₃	9.06	9.00	73.78	72.30	—	—	346.4
[Gd(QNO) ₇](ClO ₄) ₃	10.80	10.69	70.12	69.02	20.18	20.29	358.7
[Dy(QNO) ₇](ClO ₄) ₃	10.85	11.01	70.01	68.77	—	—	344.2
[Ho(QNO) ₇](ClO ₄) ₃	11.11	11.15	69.91	68.65	—	—	351.1
[Er(QNO) ₇](ClO ₄) ₃	11.28	11.29	69.90	68.55	—	—	358.3
[Yb(QNO) ₇](ClO ₄) ₃	11.67	11.64	69.63	68.28	—	—	360.1

* Molar conductance in acetonitrile.

Table 1b. Analytical and molar conductance data for iso-QNO complexes.

Complex	% Metal		% Ligand		% ClO ₄ ⁻		λ _m [*] (ohm ⁻¹ cm ² mole ⁻¹)
	Found	Calculated	Found	Calculated	Found	Calculated	
<i>Iso-quinoline-2-oxide complexes</i>							
[La(isoQNO) ₇](ClO ₄) ₃	9.43	9.56	69.50	69.91	20.42	20.55	345.9
[Pr(isoQNO) ₇](ClO ₄) ₃	9.55	9.68	69.60	69.79	—	—	341.0
[Nd(isoQNO) ₇](ClO ₄) ₃	9.73	9.89	69.83	69.63	—	—	354.1
[Gd(isoQNO) ₇](ClO ₄) ₃	10.77	10.69	69.22	69.02	—	—	358.5
[Dy(isoQNO) ₇](ClO ₄) ₃	11.11	11.01	68.57	68.77	—	—	352.8
[Ho(isoQNO) ₇](ClO ₄) ₃	11.32	11.16	68.70	68.66	—	—	348.3
[Er(isoQNO) ₇](ClO ₄) ₃	11.10	11.29	68.58	68.55	—	—	355.9
[Yb(isoQNO) ₇](ClO ₄) ₃	11.71	11.64	68.12	68.28	—	—	357.8

Bruker WH-270 spectrometer operating in the FT mode, using CD₃CN as solvent and TMS as the internal standard (table 3).

Electronic spectra of Nd³⁺, Ho³⁺ and Er³⁺ complexes in acetonitrile were recorded in the visible region on a Beckmann Model-25 spectrophotometer. The spectra for the same complexes in nujol mull were recorded in the same region on a Unicam SP-700 instrument (table 4). Electrolytic conductance measurements in acetonitrile solutions of the complexes were carried out in a Siemen's conductance bridge using an immersion cell (type LTA), previously calibrated with standard KCl solution. The concentrations of the solutions used were of the order of 10⁻³ M (table 1).

3. Results and discussion

The analytical and conductivity data are presented in table 1. The complexes have the compositions Ln(QNO)₈(ClO₄)₃ where Ln = La, Pr, and Nd, and Ln(QNO)₇(ClO₄)₃ where Ln = Gd, Dy, Ho, Er and Yb. The complexes were analysed for the formulae Ln(isoQNO)₇(ClO₄)₃ where Ln = La, Pr, Nd, Gd, Dy, Ho, Er and Yb. All the complexes are soluble in polar solvents such as methanol and acetonitrile. They are insoluble in chloroform and in nonpolar solvents such as benzene and carbon tetrachloride. Molar conductance of the complexes are in line with 1:3 electrolytes (Geary 1971) suggesting thereby that the perchlorate is monovalent ionic.

The IR spectral data are presented in tables (2a, b). The appearance of two bands, one in the region 628–630 cm⁻¹ and the other in the range 1095–1115 cm⁻¹ in the spectra of both QNO and isoQNO complexes, reveals the presence of perchlorate groups in these complexes. The bands are assigned to ν₄ and ν₃ respectively of T_d perchlorate group. Thus the IR spectra pertaining to the vibrations in both QNO and isoQNO complexes are in line with the 1:3 electrolyte behaviour of these complexes in acetonitrile solution.

Table 2a. Important IR frequencies (in cm⁻¹) and their assignments for QNO complexes.

Ligand	La	Pr	Nd	Gd	Dy	Ho	Er	Yb	Assignment
QNO									
1580 m	1588 m	1590 m	1588 w	1590 m	1588 m	1590 m	1590 m	1590 m	C=N stre
1318 m	1318 w	1326 w	1320 vw	1330 vw	1320 w	1325 vw	1330 vw	1333 w	N-O stre
1275 m	1275 m	1275 m	1276 w	1278 m	1275 m	1275 m	1275 m	1275 m	
1235 m	1238 m	1240 m	1238 w	1240 m	1237 m	1239 m	1240 m	1239 m	N-O stre
1145 m	1155 m	1156 m	1155 vw	1156 m	1155 m	1155 m	1155 m	1155 m	N-O
									other bands
									istic of N
—	1105 s	1106 s	1103 m	1105 s	1100 s	1100 s	1100 s	1100 s	ν ₃ ClO ₄ ⁻
801	808 m	815 m	808 m	818 m	818 m	817 m	818 m	818 m	C-H out-
729	734 m	732 m	732 w	735 m	732 m	732 m	735 m	732 m	
—	629 m	629 m	629 m	629 m	629 m	630 m	628 m	630 m	ν ₄ ClO ₄ ⁻

Table 2b. Important IR frequencies (in cm^{-1}) and their assignments for iso-QNO complexes.

Ligand iso-QNO	La	Pr	Nd	Gd	Dy	Ho	Er	Yb	Assignment
1580 m	1582 w	1582 w	1587 w	1582 vw	1582 w	1585 w 1560 vw	1582 vw	1587 w 1567 w	C=N stretch
1502 w	1510 w	1510 w	1510 w	1512 w	1508 w	1507 m	1509 w	1509 s	Ring stretch
1338 s	1345 m	1348 m	1356 m	1345 m	1345 m	1345 m	1346 m	1347 s	N-O deformation (other band characteristic of N-O mode)
1260 m	1260 m	1260 m	1263 m	1260 m	1260 m	1260 m	1263 m	1262 m	C-H in-plane vibration*
1218 s	1220 m	1220 m	1220 m	1223 m	1220 m	1220 m	1221 m	1222 m	N-O stretch† (νNO)
1192 s	1180 s	1181 s	1183 s	1181 s	1181 s	1183 s	1184 s	1185 s	ν_3 perchlorate
—	1100 s	1110 s	1108 s	1110 s	1110 s	1110 s	1110 s	1110 s	$\delta\text{N-O}^\dagger$
827 s	820 s	820 s	825 s	820 s	820 s	820 s	820 s	822 s	C-H out-of-plane vibration
740 m	742 s	742 s	746 s	742 s	742 s	745 s	746 s	747 s	ν_4 perchlorate
—	630 m	630 m	628 m	630 m	628 m	625 m	626 m	627 m	

* assigned as per data given for the ligand (Shindo 1960); † assigned as per data given for the ligand (Nelson *et al* 1968); s—strong; m—medium; w—weak; vw—very weak.

Table 3. Important proton NMR spectral data for QNO, iso-QNO and their La^{+3} complex in acetonitrile.

Compound	Chemical shifts in ppm with respect to tetramethyl silane							
	1H	2H	3H	4H	5H	6H	7H	8H
QNO	—	8.4857	7.4557	7.8220	7.8190	7.6823	7.7766	8.4857
La^{3+} QNO complex	—	9.0391	7.2607	7.5798	7.9374	7.4505	7.5911	8.4857
Iso-QNO	8.7341	—	8.0490	7.6010	7.8102	(5, 6,	7, 8 H)	
La^{3+} iso-QNO complex	9.0048	—	8.3167	7.6497	7.7730	(5, 6,	7, 8 H)	

Table 4. Electronic spectral data in the visible region for Nd^{3+} , Ho^{3+} and Er^{3+} complex of QNO and iso-QNO.

Nd^{3+}			Ho^{3+}			Er^{3+}		
<i>J</i> level	Energy (KK)		<i>J</i> level	Energy (KK)		<i>J</i> level	(Energy KK)	
	QNO	Iso-QNO		QNO	Iso-QNO		QNO	Iso-QNO
$^4G_{9/2}$	19.53	19.60	3K_6	24.01	23.98	$^4F_{5/2}$	22.32	22.17
$^{*4}G_{7/2}$	19.04	19.12	$^{*5}F_1, ^5G_6$	22.11	22.13	$^4F_{7/2}$	20.53	20.45
$^{*4}G_{5/2}, ^2G_{7/2}$	17.10	17.19	$^5S_2, ^5F_4$	18.62	18.60	$^{*2}H_{11/2}$	19.14	19.18
			5F_5	15.60	15.66	$^4F_{9/2}$	15.33	15.20
	$\beta = 0.9899$	0.9958		$\beta = 0.9959$	0.9968		$\beta = 0.9969$	0.9989
	$\delta = 1.0203$	0.5328		$\delta = 0.4117$	0.3210		$\delta = 0.3109$	0.1101

* β and δ have been calculated for the starred *J* levels, for which comparable aquo values are available. KK—kilokaiser.

The $\nu_{\text{N-O}}$ for QNO and its complexes splits into two bands at 1318 cm^{-1} and 1275 cm^{-1} . The splitting is attributed to a strong coupling of $\nu_{\text{N-O}}$ with other vibrations of QNO (Shindo 1960). According to Nelson *et al* (1968) however the 1235 cm^{-1} band is probably due to $\nu_{\text{N-O}}$. The IR spectra of QNO complexes, show little shift of $\nu_{\text{N-O}}$. In fact, there is a little shift to higher frequencies of $\nu_{\text{N-O}}$ in many of the complexes, probably due to the impure nature of the $\nu_{\text{N-O}}$. However the N—O deformation band at 1145 cm^{-1} , the C—H out-of-plane vibration at 729 and 801 cm^{-1} and the $\nu_{\text{C=N}}$ band at 1580 cm^{-1} all shift to higher wave numbers in the IR spectra of the QNO complexes, indicating thereby the coordination of N-oxide oxygen to the metal ion,

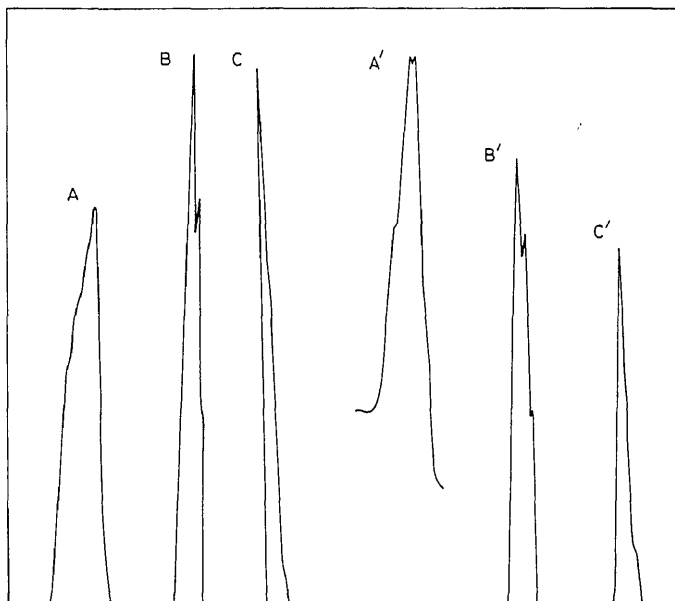
The band appearing at 1192 cm^{-1} assigned to the N—O stretching frequency in isoQNO (Clemo and Daglish 1950; Kluiber and Horrocks 1966; Nelson *et al* 1968) shifts to the lower frequency by $\approx 12\text{ cm}^{-1}$ in the spectra of isoQNO complexes indicating the binding of the N-oxide oxygen to the lanthanide metal ion. The N—O deformation band at 1339 cm^{-1} , the C—H out-of-plane vibrations at 740 , 822 cm^{-1} and the $\nu_{\text{C=N}}$ band at 1580 cm^{-1} all shift to higher frequencies revealing the coordination of the N-oxide group to the metal ion.

and isoQNO complexes with La^{3+} (table 3). The various assignments in the PMR spectra of the complexes have been made as per the assignments reported by Hamm and Philipsborn (1971). The 2H and 5H signals in the QNO complex and the 1H, 3H, and 4H signals in the isoQNO complex have downfield shifts, confirming the coordination of the N-oxide moiety to the lanthanide ion. The observed deshielding is a consequence of the drainage of electron density towards the metal ion.

The electronic spectra taken in acetonitrile solution in the visible region for Nd^{3+} , Ho^{3+} and Er^{3+} complexes of QNO and isoQNO are given in figure 1. The spectral data are presented in table 4. The $f-f$ electronic transitions of the lanthanides are found to be sharp and line like. On complexation the spectra tend to show band energy shifts, compared to those of aquo ion complexes. In the complexes of QNO and isoQNO small shifts to lower frequencies are found for all the bands. The red shift is called the nephelauxetic shift and has been related to the covalency in the metal ligand bond. Sinha (1966, 1971) has defined a parameter δ , as a measure of the covalent character of the metal ligand bond, which is given by the relation,

$$\delta(\%) = [(1 - \beta)/\beta] \times 100,$$

where β is the average value of the ratio $\nu_{\text{complex}}/\nu_{\text{aquo}}$. The β and δ values calculated for QNO and isoQNO complexes are presented in table 4. The values of QNO complexes being greater than those for the isoQNO complexes point to a greater covalency in the metal ligand bond in QNO complexes than in isoQNO complexes. Karraker (1968) has



found that the shapes of the hypersensitive bands are related to the coordination number around the lanthanide ion. We find that the solid state spectral shapes (taken in Nujol mulls) of Nd^{3+} , Ho^{3+} and Er^{3+} complexes closely resemble those in solution (in acetonitrile). This indicates a similarity in coordination number in the solid state and in solution. The shapes of the hypersensitive bands of Nd^{3+} , Ho^{3+} and Er^{3+} complexes of isoQNO and Ho^{3+} and Er^{3+} complexes of QNO markedly resemble the shapes of the seven coordinate diketonate complexes of lanthanides studied by Karraker. The spectral shape of the Nd^{3+} complex of QNO however resembles those of the eight coordinate complexes reported by Karraker.

4. Conclusions

The analytical, conductance and IR data coupled with ^1H NMR data for the lanthanide complexes of QNO and isoQNO indicate the bonding of the N-oxide group of the ligands to the lanthanide ion in the complexes. Conductance data coupled with electronic spectral shapes of the complexes reveal that while QNO complexes of La^{3+} , Pr^{3+} , Nd^{3+} have eight coordinate geometry, the QNO complexes of lanthanides, where $\text{Ln} = \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}$ and Yb , and all the lanthanide complexes of isoQNO are of seven coordinate geometry around the lanthanide ion.

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Chemistry of the diphenyldithiophosphinato complexes of iron

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Abstract. Bis(diphenyldithiophosphinato)iron(II) (**2**) is synthesised by the action of $(C_6H_5)_2PS_2H$ on $FeCO_3$. Spectroscopic data show that **2** has got a distorted tetrahedral structure. The ligand field strength in **2** (5748 cm^{-1}) as determined from the diffuse reflectance spectrum is comparable to that in reduced rubredoxin (6250 cm^{-1}). The isomer shift value in the Mossbauer spectrum of **2** also is quite consistent with that reported for reduced rubredoxin and other iron(II) tetrahedral compounds. In solution and in the presence of air **2** is spontaneously oxidised to the ferric complex $[(C_6H_5)_2PS_2]_3Fe$ (**1**). The dark green **1** is reduced to the pale yellow ferrous complex **2** by the action of $NaBH_4$ in THF solution. This redox behaviour is comparable to that of rubredoxin, although the oxidised complex differs from oxidised rubredoxin in that it has got octahedral geometry compared to the tetrahedral geometry of the oxidised rubredoxin. The reaction of **1** with 2,2'-bipyridyl, NH_3 , Br_2 and NO and the Mossbauer spectra of the products are also described here.

Keywords. Iron in sulphur environments; rubredoxin; diphenyldithiophosphinate; iron(II) and iron(III) complexes; Mossbauer spectra; mixed ligand complexes.

1. Introduction

The coordination chemistry of iron in sulphur environments has attracted the attention of chemists, because many of the iron complexes of biological importance are ligated by sulphur and function as electron carriers for many of the biological reactions. The simplest among them is rubredoxin in which $Fe(II)$ is coordinated to four cysteinyl sulphurs in an essentially tetrahedral arrangement (Eaten and Lovenberg 1970). Rubredoxin undergoes reversible one-electron oxidation and reduction with a redox potential of about -57 mV . The oxidised rubredoxin, Rd_{ox} , can be reduced with dithionite to the reduced rubredoxin, Rd_{rd} .

To understand the biological chemistry of rubredoxin in detail attempts have been made to synthesise tetrahedral complexes of iron ligated by sulphur which may be compared with the structure and properties of the active site in iron-sulphur proteins. A few tetrahedral complexes have already been synthesised. These include $Fe[(SPR)_2N]_2$ (Davison and Switkes 1971), $Fe[(SPR)_2CH]_2$ (Davison and Reger 1971) etc. However, the reversible oxidation of these complexes to the corresponding $Fe(III)$ species as in the case of rubredoxin has not been demonstrated. Further, the magnitude of the ligand field in these complexes is much smaller than that in reduced rubredoxin. Bis(*o*-xylyl- α,α' -dithiolato)ferrate(II) synthesised and structurally characterised by Lane *et al* (1977) represents the closest synthetic analogue reported so far which is comparable to the

also studied and reported here.

2. Experimental

2.1. General

Reactions were carried out in an atmosphere of nitrogen wherever necessary. S were purified by standard methods. $\text{Ph}_2\text{PS}_2\text{H}$ and its sodium salt and $(\text{Ph}_2\text{PS}_2)_2\text{Fe}$ were prepared according to published procedures (Higgins *et al* 1955; Cavell *et al* 1961).

2.2. Synthesis of $(\text{Ph}_2\text{PS}_2)_2\text{Fe}$ (**2**)

Ferrous carbonate was prepared under nitrogen by reacting an aqueous solution (20 ml) of ferrous ammonium sulphate (1.6 g, 4.08 mmol) with an aqueous solution (10 ml) of anhydrous sodium carbonate (0.5 g, 4.72 mmol). To the white suspension of ferrous carbonate alcoholic solution (20 ml) of $\text{Ph}_2\text{PS}_2\text{H}$ (2.0 g, 8.0 mmol) was added. Ferrous carbonate dissolved slowly and the solution was filtered. The clear filtrate was stirred for five hours when pale yellow crystals of **2** separated out (1.3 g, 57.5%). Crystals were filtered, washed with absolute alcohol and dried in vacuum. Analysis: Calculated for $\text{C}_{24}\text{H}_{20}\text{FeP}_2\text{S}_4$: Fe 10.07; S 23.09, Found: Fe 9.84; S 22.86. Mossbauer spectrum: $\delta = 0.85$ mm/s and $\Delta E_Q = 2.82$ mm/s. Diffuse reflectance spectrum: $\lambda_{\text{max}} 5748 \text{ cm}^{-1}$.

2.3. Reaction of **1** with NaBH_4

Dry THF (20 ml) was added to a mixture of **1** (0.8 g, 0.99 mmol) and NaBH_4 (1.06 mmol) in a dry flask under nitrogen. On stirring the dark green solution turned pale green and finally a pale yellow precipitate settled down which was filtered, washed with deoxygenated alcohol and dried. The product was identified as **2** by comparison of the electronic and Mossbauer spectra.

2.4. Reaction of **1** with 2,2'-bipyridyl

Dry benzene (20 ml) was added to a mixture of **1** (0.6 g, 0.742 mmol) and 2,2'-bipyridyl (bp), (0.35 g, 2.24 mmol) under nitrogen and stirred. The dark green solution [Fe(bp)₃][(S₂PPh₂)₃] precipitated immediately. It was filtered, washed with benzene and dried. (0.9 g, 93.9%) Analysis: Calculated for $\text{C}_{66}\text{H}_{54}\text{FeN}_6\text{P}_3\text{S}_6$: Fe 4.39; N 6.61, Found: Fe 4.46; S 14.86; N 6.70. Mossbauer spectrum: $\delta = 0.27$ mm/s and $\Delta E_Q = 0.36$ mm/s.

2.5. Reaction of **1** with NH_3

To nearly 25 ml of liquid ammonia, **1** (0.4 g, 0.49 mmol) was added and stirred. The deep green solution turned yellow and then dark brown. On complete evaporation of ammonia, a brownish yellow mass was obtained. The product was washed with

and dried in vacuum. While drying ammonium was evolved from the product giving back the starting material.

2.6. Reaction of 1 with bromine

A dichloromethane solution of bromine (0.189 g in 7 ml) was added dropwise to a solution of 1 (0.8 g, 0.99 mmol) in dichloromethane (20 ml) and kept stirred overnight. After removal of the solvent the brown mass obtained was dissolved in a minimum quantity of benzene and filtered. On cooling $[(\text{Ph}_2\text{PS}_2)_2\text{FeBr}]$ crystallised out which was filtered, washed with benzene and dried (0.4 g, 63.5%). Analysis: Calculated for $\text{C}_{24}\text{H}_{20}\text{BrFeP}_2\text{S}_4$: Br 12.61; Fe 8.81; S 20.18, Found: Br 13.29, Fe 8.83; S 19.46. Mossbauer spectrum: $\delta = 0.31$ mm/s and $\Delta E_Q = 0.11$ mm/s.

2.7. Reaction of 1 with NO

Dry NO was bubbled through a solution of 1 (0.4 g, 0.49 mmol) in dry dichloromethane (20 ml) for 1 hour. The deep green solution was changed to dark chocolate brown slowly. The formation of nitrosyl complex was indicated by the IR spectrum ($\nu_{\text{NO}} 1705 \text{ cm}^{-1}$). The product, however, decomposes easily and could not be isolated.

3. Results and discussion

The ferric complex, tris(diphenyldithiophosphinato)iron(III), 1, was prepared by a metathesis reaction as reported by Cavell *et al* (1972). It is insoluble in water and ethanol, but soluble in common organic solvents except petroleum ether. The solutions in presence of air undergo decomposition slowly. The Mossbauer spectrum of 1 is reported here for the first time (figure 1a). The spectrum shows no quadrupole splitting indicating the undistorted octahedral configuration of 1 (figure 2). The isomer shift occurs at $\delta = 0.28$ mm/s relative to iron metal which confirms the +3 oxidation state of iron and the high spin nature of the complex. The Mossbauer spectral studies of tris(dialkyldithiocarbamate)iron(III) complexes at room temperature indicate that there is a thermal equilibrium between the high and low spin states of iron(III) (Frank and Abeledo 1966). Accordingly in those cases, a quadrupole splitting is observed. The absence of quadrupole splitting in the Mossbauer spectrum of 1 confirms the absence of similar high-low spin equilibrium at room temperature.

The most important reaction undergone by 1 is that on treatment with NaBH_4 in THF solution, it is reduced to the pale yellow iron(II) complex $[(\text{C}_6\text{H}_5)_2\text{PS}_2]_2\text{Fe}$ (2). The formation of 2 is confirmed by comparison of the electronic and Mossbauer spectra with those of $[(\text{C}_6\text{H}_5)_2\text{PS}_2]_2\text{Fe}$ prepared by direct reaction *viz* by the action of $(\text{C}_6\text{H}_5)_2\text{PS}_2\text{H}$ on a freshly prepared aqueous alcoholic suspension of FeCO_3 . In solution and in presence of air 2 is spontaneously oxidised to the dark green 1. This redox behaviour is comparable to that of rubredoxin, although the oxidised complex differs from oxidised rubredoxin in that it has octahedral geometry compared to the tetrahedral geometry of the oxidised rubredoxin.

Although a tetrahedral structure has been proposed for 2 (Cavell *et al* 1972), no

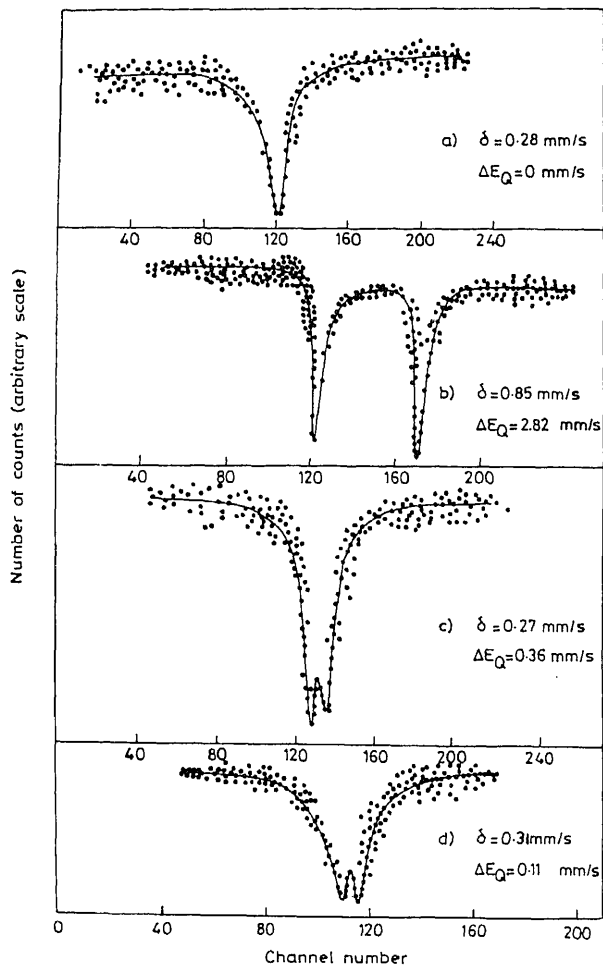
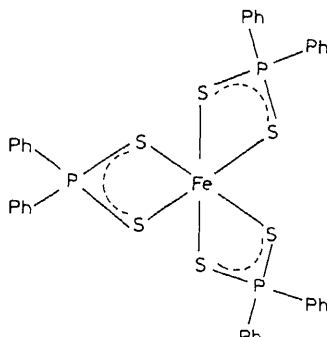


Figure 1. Mössbauer spectra at room temperature of (a) $[(\text{Ph}_2\text{PS}_2)_3\text{Fe}]$, (b) $[(\text{Ph}_2\text{PS}_2)_2\text{Fe}]$ (c) $[\text{Fe}(\text{bp})_3](\text{S}_2\text{PPh}_2)_3$ and (d) $[(\text{Ph}_2\text{PS}_2)_2\text{FeBr}]$.



complex, there is a single peak in the near infrared region corresponding to the ${}^5T_2 \leftarrow {}^5E$ transition. The absorption maximum occurs at 5748 cm^{-1} as is characteristic of iron(II) tetrahedral complexes. This is comparable to the ligand field in reduced rubredoxin (Lowe and Lovenberg 1970) which occurs at 6250 cm^{-1} and in the thiolato complex, $(o\text{-xylyl-}\alpha\text{-}\alpha'\text{-dithiolato})\text{ferrate(II) anion}$ (Lane *et al* 1977) at 5560 cm^{-1} . The peak at 5748 cm^{-1} is split indicating the tetragonal distortion from the perfect tetrahedral structure. The large splitting observed indicates that the degeneracy of the T_2 state is removed not only by spin orbit coupling but also by the Jahn-Teller effects.

The Mossbauer spectrum of **2** (Figure 1b) shows a quadrupole splitting ($\Delta E_Q = 2.82\text{ mm/s}$) centred at $\delta = 0.85\text{ mm/s}$ relative to iron metal. The isomer shift value is quite consistent with that reported for other iron(II) tetrahedral compounds and for reduced rubredoxin (Lane *et al* 1977). The observed quadrupole splitting confirms the distorted tetrahedral configuration. In perfect cubic symmetry, tetrahedral iron(II) complexes cannot exhibit quadrupole splitting since the electric field gradient at the nucleus due to the d orbitals are equal and opposite in sign. In a tetrahedral ligand field, the free ion 5D term splits into a lower 5E and an upper 5T_2 states. The energy separation between 5E and 5T_2 states is of the order of 5748 cm^{-1} . This splitting is sufficiently large that one may ignore the effect of the population of the 5T_2 state when considering the electric field gradient at the nucleus. If $[(C_6H_5)_2PS_2]_2Fe$ were exactly cubic, then the $3d$ electron outside the $3d^5$ shell would be distributed equally among the five degenerate 5E orbitals. This would produce zero quadrupole splitting, since the electric field gradient for the d_{z^2} and $d_{x^2-y^2}$ states are $-(4/7)\langle r^{-3} \rangle 3d$ and $+(4/7)\langle r^{-3} \rangle 3d$ respectively (Edwards *et al* 1967). The observation of large quadrupole splitting shows that these levels must be split by a distortion of the iron.

The reaction of **1** with 2,2'-bipyridyl (bp) in 1:3 molar ratio gives a dark red product, bis(bipyridyl)iron(III) diphenyldithiophosphinate. The Mossbauer spectrum of the product (figure 1c) shows a quadrupole splitting ($\Delta E_Q = 0.36\text{ mm/s}$) centred at $\delta = 0.27\text{ mm/s}$ relative to iron metal. These values confirm that iron is in the +3 oxidation state and that the complex is low spin. In the IR spectrum of this complex there is a medium intensity band at 1025 cm^{-1} with a shoulder at 1065 cm^{-1} due to the $\nu_s(P-S)$ and $\nu_s(P-S)$ vibrations. Further the absence of a band characteristic of Fe-S linkage expected in the region $350\text{--}380\text{ cm}^{-1}$ is due to the non-bonded nature of the $(C_6H_5)_2PS_2$ -moiety. The reaction of **1** with liquid ammonia gives a brownish yellow product, probably the hexamine complex, $[Fe(NH_3)_6](S_2PPh_2)_3$. However, while drying in vacuum, the product gives off ammonia giving back the original complex. The reaction of **1** with NO was carried out to obtain the nitrosyl complex $[(C_6H_5)_2PS_2]_2FeNO$. The formation of a chocolate brown nitrosyl complex is indicated by the IR spectrum ($\nu_{NO} 1705\text{ cm}^{-1}$). The product, however, decomposes readily and could not be isolated.

A mixed ligand complex, $[(C_6H_5)_2PS_2]_2FeBr$, is formed by the action of bromine on iron methylenechloride in a 1:1 molar ratio. The Mossbauer spectrum of the new complex (figure 1d) shows a two-line quadrupole pattern ($\Delta E_Q = 0.11\text{ mm/s}$) centred at $\delta = 0.31\text{ mm/s}$ relative to iron metal. The splitting arises due to the electric field gradient produced by different ligands. In the IR spectrum of the complex, the band at 200 cm^{-1} can be assigned to the Fe-Br vibration. The stretching frequency of Fe-S is shifted to higher frequency compared to that in $Fe(S_2PPh_2)_3$ and occurs at 380 cm^{-1} . A distorted square pyramidal structure is proposed for the complex $[(C_6H_5)_2PS_2]_2FeBr$.

analogous to bromobis(N,N'-dialkyldithiocarbamato)iron(III) complexes (Martin and White 1967).

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Absorption spectral studies on the adduct formation between $U(TTA)_4$ and some neutral donors†

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Abstract. Synergism in solvent extraction of metal ions is known to be due to adduct formation which occurs in the organic phase. The adduct formation between $U(TTA)_4$ and different neutral donors was studied by spectrophotometry. Spectral changes were used to calculate adduct formation constants (β) and values of $\log \beta$ obtained for different donors.

Keywords. Synergism; $U(TTA)_4$; neutral donor adducts.

1. Introduction

Synergism observed in the extraction of the tetravalent actinides into organic solvents containing a mixture of a β -diketone and a neutral donor, is attributed to the adduct formation between metal β -diketonate and the neutral donor. The adduct formation is usually studied by solvent extraction methods. As the adduct formation occurs in the organic phase and as the metal chelates and their adducts with neutral donors have distinct absorption spectra, spectrophotometric methods can be employed for studying the same. The stoichiometry and the formation constants of the resulting adducts can be calculated from the absorption spectral data. Such studies for the adduct formation of $U(TTA)_4$ with various monodentate neutral donors have been reported recently (Patil *et al* 1979; Patil and Ramakrishna 1979; Ramakrishna *et al* 1980; Ramanujan *et al* 1982; Bullock and Sweatman 1982). In continuation the present work was carried out to study the influence of the variation of the side chains in the monodentate neutral phosphate donors on the adduct formation constant. The monodentate donors studied are tri-butylethylphosphate (TБEP), tris-2-ethylhexylphosphate (TEHP), tridichloropropylphosphate (TDCPP) and triisobutylphosphate (TIBP). Also the absorption spectral studies on the adduct formation between $U(TTA)_4$ and bidentate neutral donors *viz* dibutyl N-N-diethyl carbamoyl methylene phosphonate (DBDECMP), bipyridyl and *o*-Phenanthroline have been carried out to determine the stoichiometry and the coordination in the adducts formed.

2. Experimental

2.1 Materials

$U(TTA)_4$ was prepared as described in literature (Prasad and Baskin 1966). Thenoyltrifluoroacetone (HTTA) and *o*-Phenanthroline were obtained from M/s

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E Merck, Germany. TBEP, TEHP, TDCPP and TBP were obtained from Tenneco Organic Ltd., Bristol. Bipyridyl was obtained from BDH, England. DBDECMP was obtained from Richmond Organics, USA.

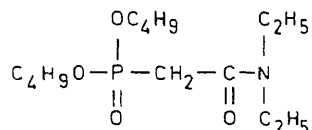
2.2 Procedure

Weighed amounts of $U(THA)_4$ and HTTA were dissolved in benzene to get a solution of $U(THA)_4$ with ten-fold excess of HTTA. Stock solutions of suitable concentration of the desired neutral donors (S) were prepared by dissolving a weighed amount of the donor in benzene. Solutions for recording the spectra were obtained by adding different aliquots of the donor stock solution to a fixed volume of $U(THA)_4$ solution and finally making up to a constant volume, in each case with benzene. Thus the U(IV) concentration in all the solutions was held constant while the concentration of the neutral donor was varied. Absorption spectra of these solutions in the visible region were recorded on CARY-14 spectrophotometer using benzene as the blank. HTTA and the neutral donors used do not absorb in this wavelength region. The absorbance values recorded at a few different wavelengths were used for the calculation of the adduct formation constants.

3. Results and discussion

3.1 Bidentate donors

$U(THA)_4$ forms a 1:1 adduct with most of the monodentate neutral donors giving a nine-coordinated species. The adduct formation of $U(THA)_4$ with a bidentate donor was studied to see whether a 10-coordinated species would be formed. Three bidentate donors viz DBDECMP, *o*-phenanthroline and bipyridyl were chosen for this study. When *o*-phenanthroline was added to the solution of $U(THA)_4$, the colour of the solution changed and the absorption values continuously decreased with time. The solution finally became yellow which suggested the oxidation of U(IV) to U(VI). The addition of bipyridyl also resulted in the oxidation of U(IV) to U(VI). The oxidation of U(IV) is apparently a consequence of the stronger adduct forming tendency of these neutral donors with $UO_2(THA)_2$ than with $U(THA)_4$. Hence the studies were restricted to DBDECMP which did not cause the oxidation of $U(THA)_4$. The structure of DBDECMP has been shown below:



The spectral changes of $U(THA)_4$ on the addition of various amounts of DBDECMP are shown in figure 1. The changes are similar to those observed with all other monodentate donors. This indicated that DBDECMP behaves as a monodentate donor during adduct formation with $U(THA)_4$.

The monoadduct formation equilibrium is given as (S = neutral donor),

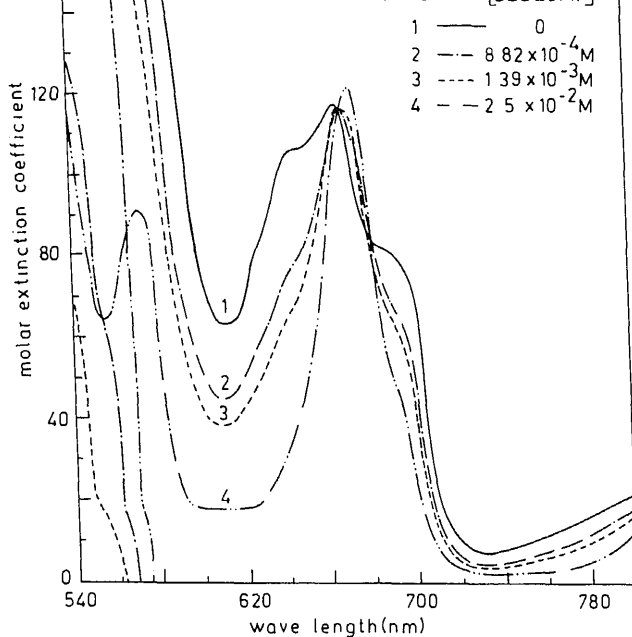


Figure 1.

The adduct formation constant (β) can be written as

$$\beta = \frac{[U(TTA)_4 \cdot S]}{[U(TTA)_4][S]_{\text{free}}} = \frac{(E_1 - E)}{(E - E_2)[S]_{\text{free}}}, \quad (2)$$

where E_1 , E_2 and E are molar extinction coefficients of $U(TTA)_4$, $U(TTA)_4 \cdot S$ and their mixture, respectively, at a particular wavelength. The concentration of free neutral donor $[S]_{\text{free}}$ is given by

$$[S]_{\text{free}} = [S]_{\text{total}} - \frac{(E_1 - E) \cdot C}{(E_1 - E_2)}, \quad (3)$$

where C is the total concentration of $U(IV)$. The value of E_2 at the desired wavelength was obtained from the absorbance of $U(TTA)_4$ in the presence of a large excess of the donor and it was assumed that $U(TTA)_4$ was completely converted to $U(TTA)_4 \cdot S$. This assumption was confirmed as no change was seen in the spectrum on further increasing the donor concentration. From the known values of E_1 , E_2 , E , C and $[S]_{\text{total}}$ the β values are calculated. Table 1 gives the β values calculated for DBDECMP at various concentrations of donor and at different wavelengths. The magnitude of the average β value ($\log \beta = 3.2$) is of the same order as that of a monodentate phospho-donor such as TBP. This is in confirmation with our earlier conclusion obtained from the spectral changes *viz* that this donor behaves as a monodentate donor towards $U(TTA)_4$.

Table 1. Spectrophotometric data on the adduct formation between U(TTA)₄ and DBDECMP in benzene.

[DBDECMP]	Molar extinction coefficient							
	(E) at wavelength (nm)				log β at wavelength (nm)			
[U(TTA) ₄]	560	570	580	590	560	570	580	590
0 (E ₁)	264	177	128	90	—	—	—	—
80 (E ₂)	85	86	44	20	—	—	—	—
0.7	193	146	96	63	3.25	3.07	3.18	3.18
0.9	178	146	93	61	3.25	2.88	3.05	3.07
1	170	133	85	54	3.28	3.16	3.22	3.21
1.2	160	128	81	51	3.26	3.15	3.20	3.19
1.5	148	121	74	46	3.24	3.14	3.21	3.14

$$[U(IV)] = 1.25 \times 10^{-3} \text{ M.}$$

Table 2. β-values with different donors.

Donor (S)	log β
TDCPP	1.3
TBEP	2.3
TEHP	2.8
TIBP	3.0

3.2 Monodentate donors

In continuation of earlier work four additional neutral monodentate donors were taken up for study. The spectral changes on the addition of each of these donors to U(TTA)₄ were similar to monoadduct spectra. For TDCPP and TIBP the β values were calculated from the spectral data as described for DBDECMP. Such calculation however was not possible with TEHP and TBEP as obtaining E₂ values required the use of higher concentrations of these donors which induced partial oxidation of U(IV) in the solution. Hence an alternative method (Hershenson *et al* 1953), which does not require the knowledge of E₂ for β calculation, was used. The method used involves the following expression which is obtained on rearranging (2):

$$[S]_{\text{free}}/(E_1 - E) = 1/\beta(E_2 - E_1) + [S]_{\text{free}}/(E_2 - E_1). \quad (4)$$

The plot of $[S]_{\text{free}}/(E_1 - E)$ vs $[S]_{\text{free}}$ will give a straight line and slope/intercept will give the β values. To use this method $[S]_{\text{total}}$ was taken as an initial approximation of $[S]_{\text{free}}$. The corrected $[S]_{\text{free}}$ was calculated iteratively from the plot and using the expression:

$$[S]_{\text{free}} = [S]_{\text{total}} - (E_1 - E) \cdot C \cdot \text{slope}. \quad (5)$$

With TEHP and TBEP only 3 iterations were required to reach constant $[S]_{\text{free}}$ values. β values were calculated from the plot using corrected $[S]_{\text{free}}$ values. Table 2 summarizes

data taken from literature) were found to be the same thus suggesting that the isopropyl group has not offered any steric hindrance to the donor. Substitution of the chloro group in the side-chain (TDCPP) has lowered the adduct stability appreciably by lowering the basicity of the donor.

Acknowledgement

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Study of the probable reason why Ni(II) is excluded from metalloenzymes

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Abstract. The formation constants of the complexes of the type $[\text{NiAL}]$, where $A = 2,2'$ -bipyridyl, 1,10-phenanthroline, 2-(2'-pyridyl) benzimidazole, or 2-(2'-pyridyl) imidazoline and $L =$ ethylenediamine, 1,2-diaminopropane, N-methyl-ethylenediamine, glycine, α -alanine, β -alanine, malonate, histidine, or histamine have been determined in dioxan-water (1:1 v/v) medium and $\mu = 0.2 \text{ mol dm}^{-3} \text{ NaClO}_4$ at 30°C . The values of $\Delta \log K_M$ ($\log K_{MAL}^{\text{MA}} - \log K_{ML}^{\text{M}}$) in Ni(II) complexes have been compared with corresponding Cu(II) complexes. It is observed that for $[\text{NiAL}]$ complexes, where $L = L^1$ to L^7 , $\Delta \log K$ is more negative than for the corresponding $[\text{CuAL}]$ complexes whereas in cases where $L = L^8$, or L^9 , $\Delta \log K$ for Ni(II) complexes is less negative than for the corresponding Cu(II) complexes. The reason has been discussed.

Keywords. Mixed-ligand complexes with histidine; mixed-ligand complexes with histamine; complexes with heteroaromatic N-bases; mixed-ligand complexes of Ni(II).

Introduction

It has been observed (Sigel 1967; Bhattacharya and Chidambaram 1970; Griesser and Sigel 1970) that in the complexes $[\text{CuA}]$, where $A = 2,2'$ -bipyridyl or 1,10-phenanthroline, there is $\text{Cu} \rightarrow A$ π interaction, resulting in the increase in class A character of Cu(II) in $[\text{CuA}]$, with consequent discriminating behaviour of $[\text{CuA}]$ for ligands with N-N, $\text{O}^- - \text{N}$ and $\text{O}^- - \text{O}^-$ coordination (Griesser and Sigel 1970; Sigel 1970; Prijs and Sigel 1975; Bhattacharya *et al* 1982a). There is maximum stabilization of $[\text{CuA O}^- - \text{O}^-]$ complexes. This has been ascribed to the increase in class A character of $[\text{CuA}]$ (Griesser and Sigel 1970) in the ternary complexes, with consequent release of repulsion between metal ion $d\pi$ electrons and the lone pairs of electrons over the O^- of ligands (Bhattacharya *et al* 1982b).

Kruck and Sarkar (1973) and Bhattacharya and Patel (1984) observed that Cu(II) forms two types of complexes with histidine in aqueous medium, $[\text{Cu}(\text{H. Hist})]$ with coordination from the amino carboxylate end, the imidazole nitrogen being free and protonated, and $[\text{Cu}(\text{Hist})]$, with coordination from the amino nitrogen, the imidazole nitrogen and carboxylate. At very low pH i.e. $1.8 \sim 3.2$, there is formation of a $[\text{Cu}(\text{H. Hist})]$ species involving glycine-like coordination and the imidazole nitrogen remains protonated. At pH 4.1–6.0, there is coordination of the second histidinate moiety Hist or H. Hist respectively, resulting in the formation of $[\text{Cu}(\text{Hist})(\text{H. Hist})]$, where one tridentate histidine molecule binds to Cu(II) through

binds like glycine, i.e. through the amino nitrogen and carboxyl oxygen, the imidazole nitrogen remaining free and protonated. At still higher pH there is formation of $[\text{Cu}(\text{Hist})_2]$ with two tridentate histidines.

In ternary complexes of Cu(II) containing aromatic tertiary amines A and histidine, both $[\text{CuA}(\text{H.Hist})]$ and $[\text{CuA}(\text{Hist})]$ species are formed in aqueous medium (Bhattacharya *et al* 1984), and $\Delta \log K$ is less negative for $\text{O}^- - \text{N}$ coordinating $[\text{CuA}(\text{H.Hist})]$ species and more negative for $\text{N} - \text{N}$ coordinating $[\text{CuA}(\text{Hist})]$ species.

Histidine is known to coordinate with Ni(II) only as a tridentate ligand through the imidazole nitrogen, amino nitrogen and carboxylate, forming $[\text{NiL}]$ and $[\text{NiL}_2]$ species (Fraser and Harding 1967; Grant and Led 1977).

It is interesting to study the formation constants of mixed-ligand complexes $[\text{MAL}]$, where $\text{M} = \text{Ni(II)}$, $\text{A} = 2,2'$ -bipyridyl (A^1), 1,10-phenanthroline (A^2), 2-(2'-pyridyl)-benzimidazole (A^3), 2-(2'-pyridyl) imidazoline (A^4) and $\text{L} =$ ethylenediamine (L^1), 1,2-diaminopropane (L^2), N-methylethylenediamine (L^3), glycine (L^4), α -alanine (L^5), β -alanine (L^6), malonate (L^7), histidine (L^8), or histamine (L^9). In order to compare the stabilities of the ternary complexes with those of Cu(II), the formation constants of the mixed-ligand complexes $[\text{CuAL}]$, where $\text{L} = \text{L}^1$ to L^7 , have been taken from our earlier work (Bhattacharya *et al* 1982a). For $[\text{CuAL}]$ complexes where $\text{L} = \text{L}^8$, or L^9 , the formation constants are known in aqueous medium (Bhattacharya *et al* 1984) but the values were redetermined in 50% dioxan-water (1:1 v/v) medium, for comparison with Ni(II) complexes under identical conditions.

2. Experimental

All reagents used were of AR grade, except 2-(2'-pyridyl)-benzimidazole and 2-(2'-pyridyl) imidazoline, which were prepared by known methods (Freiser and Walter 1954).

The proton-ligand and metal-ligand formation constants were determined by normal Irving-Rossotti titration techniques (Irving and Rossotti 1953, 1954). The titrations were carried out on solutions containing Ni(II):A:L in 1:1:1 and 1:1:10 ratio, for mixed-ligand complexes $[\text{NiAL}]$ where, $\text{L} = \text{L}^1 - \text{L}^7$, to determine formation constants $\log K_{\text{NiAL}}^{\text{NiA}}$ and $\log K_{\text{NiAL}_2}^{\text{NiA}}$ by using an extension of the Irving-Rossotti technique (Bhattacharya and Chidambaram 1970). In mixed-ligand complexes $[\text{NiAL}]$, where $\text{L} = \text{L}^8$, or L^9 , only the species $[\text{NiAL}]$ is formed with coordination through imidazole and the amino nitrogen and hence, the formation constant of the species $[\text{NiAL}]$ was determined.

The values of proto-ligand and binary metal-ligand formation constants were subjected to refinement by using the computer program scogs (Sayce 1968, 1971; Sayce and Sharma 1972) as discussed earlier (Bhattacharya *et al* 1982a), and the values are given in table 1. The refinement was carried out in two ways by considering

- (i) species present in the solution to be LH_2 , LH , L , $[\text{NiA}]$ and $[\text{NiAL}]$ and $[\text{NiAL}_2]$, where $\text{L} = \text{L}^1$ to L^7 ,
- (ii) all possible species present in the solution i.e. LH_2 , LH , L , AH_2 , AH , A , $[\text{NiL}]$, $[\text{NiL}_2]$, $[\text{NiL}_3]$, $[\text{NiA}]$, $[\text{NiA}_2]$, $[\text{NiAL}]$ and $[\text{NiAL}_2]$, where $\text{L} = \text{L}^1$ to L^7 .

In $[\text{NiAL}]$ complexes, where $\text{L} = \text{L}^8$, or L^9 , formation of $[\text{NiAL}_2]$ species was not

Ligand	K_1^H	K_2^H	K_3^H	$\log K_{NiL}^{Ni}$	$\log K_{NiL_2}^{NiL}$	$\log K_{NiL_3}^{NiL_2}$
L^1	9.72 (0.03)	6.98 (0.04)	—	8.83 (0.08)	7.34 (0.13)	7.26 (0.18)
L^2	9.26 (0.03)	6.35 (0.03)	—	8.94 (0.12)	7.03 (0.11)	5.92 (0.15)
L^3	9.64 (0.03)	6.89 (0.04)	—	7.58 (0.10)	6.23 (0.09)	4.38 (0.16)
L^4	9.71 (0.01)	3.29 (0.01)	—	7.27 (0.07)	5.70 (0.08)	4.57 (0.10)
L^5	9.43 (0.01)	3.38 (0.01)	—	6.28 (0.08)	5.14 (0.08)	4.58 (0.10)
L^6	9.81 (0.04)	4.48 (0.00)	—	5.90 (0.10)	4.21 (0.10)	2.36 (0.26)
L^7	7.09 (0.07)	4.20 (0.10)	—	7.27 (0.11)	6.60 (0.10)	3.29 (0.20)
L^8	9.14 (0.07)	5.90 (0.10)	2.93 (0.10)	10.19 (0.06)	7.93 (0.09)	—
L^9	9.47 (0.06)	5.62 (0.08)	—	6.99 (0.08)	4.76 (0.20)	3.48 (0.30)

idered, because this did not lead to convergence in computer calculations. is probably because of steric hindrance, and hence the species considered were LH_2 , LH , L , $[NiA]$ and $[NiAL]$ in the first computer method and LH_3 , LH_2 , LH , H_2 , AH , A , $[NiA]$, $[NiA_2]$, $[NiL]$, $[NiL_2]$ and $[NiAL]$ in the second.

binary Cu(II)-histidine complexes, in 50% dioxan-water (1:1 v/v) medium, the es $[CuL]$, $[CuLH]$, $[CuL(LH)]$ and $[CuL_2]$ were considered to be formed and ergence was obtained. However, in the ternary system, in 50% dioxan-water v/v) medium, no protonated mixed-ligand species $[CuA(LH)]$ was considered ce in aqueous medium (Bhattacharya *et al* 1984), because protonated species do not to convergence. The non-existence of the species $[CuA(LH)]$ may be because in an-water medium, the protonation of the imidazole nitrogen is weak and hence the on dissociates in the lower pH range. Hence, histidine coordinates with $[CuA]$ ough the imidazole nitrogen and the amino nitrogen resulting in the formation of $[CuAL]$. The formation constant of $[CuAL]$ was determined by the two computer ods considering the same species as in Ni(II) complexes. The values are reported in 2.

Results and discussion

interesting to observe that in ternary complexes of Ni(II), the value of the mixed- d formation constant $\log K_{NiAL}^{NiA}$ obtained by the first computer method, assuming

Table 2. Binary complex formation constants of copper(II) in 50% dioxan-water (1:1 v/v) medium, with 0.2 M NaClO₄ and at 30°C, refined by the computer method, with standard deviation 6β in parentheses.

Binary complex formation constants of Cu(II)				
Ligand	$\log K_{\text{CuLH}}^{\text{Cu}}$	$\log K_{\text{CuL}}^{\text{Cu}}$	$\log K_{\text{CuL(LH)}}^{\text{Cu}}$	$\log K_{\text{CuL}_2}^{\text{Cu}}$
L ⁸	9.94 (0.10)	11.43 (0.04)	8.28 (0.20)	8.15 (0.03)
L ⁹	—	9.97 (0.30)	—	8.54 (0.50)

Note: For ligand L = L¹ to L⁷ see Bhattacharya *et al* (1982a).

the formation of the complex in steps, $\text{Ni} + \text{A} \rightleftharpoons [\text{NiA}]$ and $[\text{NiA}] + \text{L} \rightleftharpoons [\text{NiAL}]$, and the value obtained by the second computer method, assuming simultaneous coordination of A and L, are nearly equal. This shows that $[\text{NiA}]$ formation is almost complete in the lower pH range and in the higher pH range L combines with $[\text{NiA}]$ forming $[\text{NiAL}]$.

This is further confirmed by observing the concentrations of various species (as percentages of the total Ni(II) present) against pH in the second computer method. In the system $[\text{NiA}^1\text{L}^1]$, at the lower pH, Ni(II) and $[\text{NiA}^1]$ are the major species. After this the formation of $[\text{NiA}^1\text{L}^1]$ starts, which is maximum at pH 6.0 (61.0%), after which it decreases and the formation of $[\text{NiA}^1\text{L}^1_2]$ increases and reaches maximum (46.0%) at pH 6.7. In $[\text{NiA}^1\text{L}^4]$, the maximum percentage of the mixed-ligand complex is 62.0% at pH 6.9, after which formation of $[\text{NiA}^1\text{L}^4_2]$ increases and reaches a maximum (21.0%) at pH 8.2. In $[\text{NiA}^1\text{L}^7]$, the maximum percentage of mixed-ligand is 61.0% at pH 5.6. In $[\text{NiA}^1\text{L}^8]$, the maximum percentage of the mixed-ligand complex is 67.0% at pH 6.5, $[\text{NiA}^1]$ is 14.0%, $[\text{NiL}]$ 6.0%, and $[\text{NiL}_2]$ 13.0% at the same pH, the total being almost 100%. In $[\text{NiA}^1\text{L}^9]$, the maximum percentage of the mixed-ligand complex is 88.0% at pH 9.5.

The value of $\log K_{\text{NiAL}_2}^{\text{NiA}}$ obtained from the data of the 1:1:10 solution using the first computer method does not agree with that obtained by the second method. This is because $[\text{NiAL}_2]$ is formed at higher pH and formation of $[\text{NiL}_3]$ starts in this range. Thus, the reaction mixture does not only contain the complex species $[\text{NiA}^1]$, $[\text{NiAL}]$ and $[\text{NiAL}_2]$ as considered by the first method. A reliable value of $\log K_{\text{NiAL}_2}^{\text{NiA}}$ is obtained by the second method which considers all the possible species formed i.e. $[\text{NiA}]$, $[\text{NiA}_2]$, $[\text{NiL}]$, $[\text{NiL}_2]$, $[\text{NiL}_3]$, $[\text{NiAL}]$ and $[\text{NiAL}_2]$.

Since values obtained by the second method are more precise, they have been presented in table 4 for $\log K_{\text{NiAL}}^{\text{NiA}}$ (L = L¹ to L⁹) and $\log K_{\text{NiAL}_2}^{\text{NiA}}$ (L = L¹ to L⁷) and these have been used to interpret the data. This table also includes $\Delta \log K_{\text{M}}$ ($\log K_{\text{MAL}}^{\text{MA}} - \log K_{\text{ML}}^{\text{M}}$) for Ni(II) complexes. $\Delta \log K_{\text{M}}$ for Cu(II) complexes are also included from our earlier work (Bhattacharya *et al* 1982a) for ligands L = L¹ to L⁷, and from the present work for L = L⁸, or L⁹, for comparison.

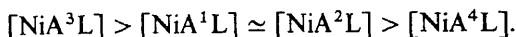
The formation constant values show that in the complex $[\text{NiAL}]$ where L

Table 3. Ternary complex formation constants of copper(II) in 50% dioxan-water (1:1 v/v) medium with 0.2 M NaClO₄ and at 30°C refined by computer method, with standard deviation $\sigma\beta$ in parentheses.

Ligand	$\log K_{\text{CuA}}^{\text{CuA}}_{\text{CuAL}}$			
	A ¹	A ²	A ³	A ⁴
L ⁸	8.80 (0.10)	8.89 (0.10)	9.33 (0.20)	9.10 (0.20)
L ⁹	8.79 (0.01)	7.99 (0.01)	9.09 (0.08)	7.38 (0.07)

Note: For L = L¹ to L⁷ see Bhattacharya *et al* (1982a).

has two O⁻ as coordinating sites like malonate (L⁷), and A = A¹, A², or A⁴, $\Delta \log K_{\text{Ni}}$ is negative, though less than N-N or O⁻-N coordinating ligands in [NiAL] complexes. In the [NiA³L⁷] complex, $\Delta \log K$ is positive. Thus, there is a statistical stabilization of ternary Ni(II) complex though not to the same extent as that in Cu(II) complexes (Bhattacharya *et al* 1982a). This can be explained as in Cu(II) complexes, by considering M $\rightarrow$ A π interaction. The stabilization of ternary complexes is in the increasing order of M $\rightarrow$ A π interaction as observed in Cu(II) complexes. The order of formation constants of ternary complexes is



It is interesting to observe that in [NiA³ O⁻-O⁻] complexes $\Delta \log K$ is positive, because the Ni $\rightarrow$ A³ π interaction is maximum. This is perhaps the first case of a positive $\Delta \log K$ observed in Ni(II) complexes.

[NiA] complexes also discriminate the ligand L in the order O⁻-O⁻ > O⁻-N > N-N, though not to the same extent as in [CuA]. This can be explained as in Cu(II) complexes, in terms of release of electron repulsion in the ternary complex. The release in repulsion is maximum in a O⁻-O⁻ ligand with lone pairs of electrons over the two O⁻. The release in repulsion is less in O⁻-N with the lone pair electrons only over O⁻. The effect is absent in N-N coordinating ligand with no lone pair electrons over the N atoms.

In [MAL] complexes, where M = Cu(II), or Ni(II) and L = L⁸, or L⁹, $\Delta \log K$ is negative as expected for a N-N coordinating ligand.

It is generally observed that $\Delta \log K_{\text{M}} (\log K_{\text{MAL}}^{\text{MA}} - \log K_{\text{ML}}^{\text{ML}})$ for Cu(II) complexes is less negative than that for Ni(II) complexes for the same ligand L (table 4). This has been explained as due to the Jahn-Teller distortion (Griesser and Sigel 1970). This is true when L = aliphatic ligands L¹ to L⁷. But in cases of [NiAL] complexes, where L = L⁸, or L⁹, coordinating through two tertiary nitrogens, $\Delta \log K$ for Ni(II) complexes is less negative than Cu(II) complexes (table 4). This leads us to the conclusion that in

Table 4. Ternary complex formation constants of nickel(II) ($\log K_{\text{NiAL}}^{\text{NIA}} = a$, $\log K_{\text{NiAL}_2}^{\text{NIA}} = b$) in 50% dioxan-water (1:1 v/v) medium with 0.2 M NaClO₄ and at 30°C, refined by computer method with standard deviation $\sigma\beta$ in parentheses, including $\Delta \log K_M$ ($\log K_{\text{MAL}}^{\text{NIA}} - \log K_{\text{ML}}^{\text{NIA}}$) for nickel(II) and copper(II) complexes.

ligand	$\log K_{\text{NiAL}}^{\text{NIA}}$	A^1 $\Delta \log K_{\text{Ni}}$	$\Delta \log K_{\text{Cu}}^*$	$\log K_{\text{NiAL}_2}^{\text{NIA}}$	A^2 $\Delta \log K_{\text{Ni}}$	$\Delta \log K_{\text{Cu}}^*$	$\log K_{\text{NiAL}_3}^{\text{NIA}}$	A^3 $\Delta \log K_{\text{Ni}}$	$\Delta \log K_{\text{Cu}}^*$	$\log K_{\text{NiAL}_4}^{\text{NIA}}$	A^4 $\Delta \log K_{\text{Ni}}$	$\Delta \log K_{\text{Cu}}^*$
<i>a</i>	7.60 (0.08)	-1.23	-1.08	7.47 (0.05)	-1.36	-1.27	7.71 (0.11)	-1.13	-0.65	6.95 (0.11)	-1.88	-1.16
<i>b</i>	6.39 (0.11)	—	—	6.46 (0.06)	—	—	—	—	—	—	—	—
<i>a</i>	7.22 (0.04)	-1.72	-1.00	7.22 (0.11)	-1.72	-0.84	7.43 (0.08)	-1.51	-0.30	6.62 (0.10)	-2.32	-0.97
<i>b</i>	5.64 (0.15)	—	—	5.64 (0.01)	—	—	—	—	—	—	—	—
<i>a</i>	5.72 (0.11)	-1.86	-1.56	5.76 (0.08)	-1.86	-1.52	6.03 (0.06)	-1.55	-0.95	5.46 (0.06)	-2.12	-1.54
<i>b</i>	5.54 (0.05)	—	—	5.65 (0.11)	—	—	—	—	—	—	—	—
<i>a</i>	6.03 (0.10)	-1.24	-0.44	6.60 (0.02)	-0.61	-0.03	6.73 (0.01)	-0.54	+0.20	4.99 (0.02)	-2.28	-1.05
<i>b</i>	4.24 (0.30)	—	—	4.24 (0.20)	—	—	—	—	—	—	—	—
<i>a</i>	5.95 (0.06)	-0.33	-0.51	5.82 (0.05)	-0.46	-0.66	6.13 (0.01)	-0.15	-0.40	4.89 (0.01)	-1.39	-1.71
<i>b</i>	4.26 (0.08)	—	—	4.21 (0.10)	—	—	—	—	—	—	—	—

L ⁶ a	5.25 (0.04)	-0.65	-0.71	4.95 (0.03)	-0.95	-0.83	5.34 (0.10)	-0.56	-0.23	4.70 (0.01)	-1.20
b	3.62 (0.05)	—	—	2.79 (0.04)	—	—	—	—	—	—	—
L ⁷ a	6.64 (0.18)	-0.63	+0.48	6.55 (0.09)	-0.72	+0.48	7.38 (0.12)	+0.11	+0.72	6.15 (0.08)	-1.12
b	4.71 (0.11)	—	—	4.73 (0.06)	—	—	—	—	—	—	—
L ⁸ a	8.35 (0.10)	-1.84	-2.63	7.93 (0.10)	-2.26	-2.54	8.61 (0.10)	-1.58	-2.10	7.23 (0.20)	-2.96
b	—	—	—	—	—	—	—	—	—	—	—
L ⁹ a	5.87 (0.10)	-1.12	-1.18	6.03 (0.10)	-0.96	-1.98	6.20 (0.40)	-0.79	-0.88	5.65 (0.40)	-1.34
b	—	—	—	—	—	—	—	—	—	—	—

* For L = L¹ to L⁷ refer Bhattacharya *et al* (1982) and for L = L⁸ or L⁹ see text.

the axial position and hence $\Delta \log K$ for Ni(II) complexes is less negative than that Cu(II) complexes (Bhattacharya *et al* 1973, 1977).

However, in [MA (histamine)] system also $\Delta \log K$ for Ni(II) is less negative than the corresponding Cu(II) complexes, though histamine is bidentate and can occupy two equatorial positions in both $[\text{Cu}(\text{histamine})]^{2+}$ and $[\text{CuA}(\text{histamine})]^{2+}$. The probable reason could be that as in $[\text{Cu}(\text{bipy})_2(\text{H}_2\text{O})_2]$, complexes with *cis* distorted structure (Sigel 1972), and the $[\text{Cu}(\text{Hist})_2]$ complex with one ligand having a histidine type of coordination in an equatorial plane and another having a histidine type N coordination, one in the equatorial and the other in the axial position $[\text{Cu}(\text{bipy})\text{L}(\text{H}_2\text{O})_2]$ (L = histidine or histamine coordinating through two tertiary nitrogens as in bipyridyl), also has a *cis* distorted structure. Hence, in the formation $[\text{Cu} \text{ bipy} (\text{Hist})]$ from $[\text{Cu} \text{ bipy} (\text{H}_2\text{O})_2]$, histidine gets coordinated at two equatorial positions (O–N) and one axial position through the imidazole N. In $[\text{CuA}(\text{histamine})]$ also the histamine nitrogens occupy one equatorial and one axial position. Due to Jahn-Teller effect, the ligand L is strained and the value of $\log K_{\text{CuA}}^{\text{CuA}}$ is lowered, resulting more negative $\Delta \log K$ values. In Ni(II) complexes, there is no Jahn-Teller distortion and hence L is not strained in the formation of *cis* $[\text{Ni} \text{ bipy} \text{ L}]$ and $\Delta \log K$ is less negative than in Cu(II) complexes.

Thus, Cu(II) bound to a tertiary amine does not prefer to coordinate with another tertiary amine molecule, but prefers to coordinate with O^- –N or O^- – O^- ligands. However, Ni(II) bound to a tertiary amine molecule does not resist combination with another tertiary amine molecule. Further, $[\text{Ni} \text{ tertiary amine}]$ also has a lesser tendency to coordinate with O^- –N or O^- – O^- ligands.

This may be extended as the probable reason for Cu(II) occurring in biological systems forming ternary complexes involving coordination of tertiary amine (imidazole, histidine, or histamine) and amino or peptide (O^- –N) or phenolate (O^- – O^-). But Ni(II) prefers to form $[\text{Ni}(\text{tertiary amine})_2]$ and hence has a lesser tendency to form $[\text{Ni}(\text{tertiary amine})\text{O}^-$ –N] or $[\text{Ni}(\text{tertiary amine})\text{O}^-$ – $\text{O}^-]$ type of complexes. Hence Ni(II) has a lesser probability of occurring in metalloenzymes involving imidazole type ligands and O^- –N or O^- – O^- coordinating ligands.

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Synthesis and analytical properties of the 5,5'-dithiodisalicylhydroxamic acid

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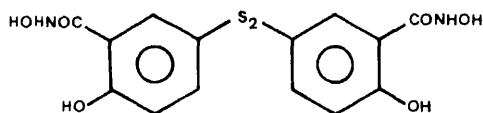
Abstract. 5,5'-dithiodisalicylhydroxamic acid (DTDSHA) has been synthesized and its solubility in water at different temperatures, spectral characteristics, and pK_a values are reported. The reactivity with inorganic ions, in aqueous media, by extraction with benzenic solution of trioctylmethylammonium chloride (Adogen 464), and on ion-exchange resins have been investigated. Its low selectivity can be increased by appropriate control of pH, the use of masking agents, or by extraction.

Keywords. Hydroxamic acid; physicochemical properties; analytical properties.

Introduction

Hydroxamic acids show a remarkable ability to form metal complexes and hence are useful reagents in inorganic analysis. Thus, many methods have been described (Majumdar 1956; Brandt 1960; Poddar *et al* 1966; Majumdar 1971; Agrawal 1980; Agrawal and Patel 1980), especially those employing benzohydroxamic and salicylhydroxamic acids, and their derivatives. Among them, extraction has an important role in the preconcentration, separation and determination of metal ions (Agrawal and Patel 1980). Recently (González-Parra 1983; Salinas *et al* 1983; Salinas and Jiménez-Gabab 1984) the extraction with benzenic or toluenic solutions of Adogen 464 (trioctylmethylammonium chloride) has been proposed for the extraction-photometric determination of several ions.

In this paper, we report the synthesis and physico-chemical properties of DTDSHA (I), as well as its complex-formation with metal ions, under varying experimental conditions.



(I)

2. Experimental

2.1 Reagents and apparatus

All solvents and chemicals used were of Analytical grade. Stock solutions of the were standardized by well known methods. Deionized water was employed purposes.

Infrared spectra were recorded with a Perkin-Elmer 297 IR spectrophotometer 4000–600 cm^{-1} range, using the KBr pellet technique. The absorption spectra solutions were obtained using a Beckman ACTA III UV-VIS spectrophotometer (quartz cells).

pH measurements were carried out with an Orion 801 pH meter equipped glass-calomel combination electrode. To determine the dissociation constants of DTDSA, the potentiometric methods of Schwarzembach *et al* (1947), Chabert (1952), Martell (1952), and Irving and Rossotti (1954), and the spectrophotometric methods described by Thamer (1955), were applied. The solubility of DTDSA in water was measured by Rose's method (1966) at several temperatures.

2.2 Synthesis of DTDSA

5,5'-dithiodisalicylic acid (225 g), synthesized employing the method of Kundra (1937) and Airan and Kulkarni (1951), was taken in ethanol (1000 ml) and concentrated sulfuric acid (70 ml) was slowly added. After refluxing the reaction mixture for 3–4 hr, benzene (250 ml) was added and the water produced in the reaction was removed by azeotrope of ethanol-water-benzene (300 ml). The process was repeated five times. The final reaction mixture was neutralized with NaHCO_3 . The diethyl ester obtained as a green-yellowish product, was extracted with benzene and was recrystallized with the same solvent. Yield 60%; m.p. $102 \pm 1^\circ\text{C}$. Elemental analysis, Found: C 54.96; H 4.60; S 16.17. Calculated: C 54.81; H 4.60; S 16.26 for $\text{C}_{18}\text{H}_{18}\text{O}_6\text{S}_2$.

The ester (5 g) was slowly added with stirring to a solution of hydroxylamine hydrochloride (3.5 g) in 12% NaOH (50 ml). The reaction mixture was allowed to stir for 24 hr, and ethanol was added to 50%. DTDSA was precipitated transferring the solid through an acid-charged cation exchange resin column (Dowex 50-X8) and evaporated ethanol. The residue was purified by recrystallization from a water-ethanol mixture. Yield 80%; m.p. $198 \pm 1^\circ\text{C}$. Elemental analysis, Found: C 46.32; H 3.24; N 7.54; S 17.41. Calculated: C 45.65; H 3.28; N 7.60; S 17.41 for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_6\text{S}_2$.

3. Results and discussion

3.1 Physicochemical properties of DTDSA

3.1a *Spectral characteristics*: The most important IR bands of DTDSA are summarized in table 1. Other hydroxamic acids (Orville-Thomas and Parsons 1958; 1961; Forteza 1981; Capitán-Vallvey *et al* 1982; Jiménez 1982; Soler *et al* 1982) show similar absorptions.

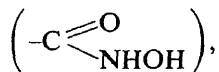
The stretching vibration frequency of the NH group (3310 cm^{-1}) and the a

Table 1. Spectral properties of DTDSA.

IR	Vibrational mode	Frequency (cm ⁻¹)
ν NH		3310 <i>s</i> *
ν C=O (amide I band)		1630 <i>vs</i>
ν OH hydroxamic		2880 <i>s</i>
ν OH phenolic		3130 <i>s, b</i>
δ NH (amide II, band)		1570 <i>s</i>
ν C-N (amide III, band)		1295 <i>m</i>
ν NO		950 <i>w</i>
UV	$\lambda_{\max}$	$\epsilon(1 \text{ mol}^{-1} \text{ cm}^{-1})$
	230 nm (water)	5.07×10^4
	220 nm (ethanol)	3.36×10^4

* *s* = strong; *vs* = very strong; *m* = medium; *w* = weak and *b* = broad.

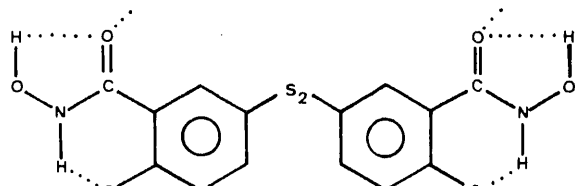
). Accordingly, it is possible to affirm that the DTDSA has, in the solid state, the ' structure



g similar to other hydroxamic acids (Exner 1968; Bracher and Small 1970; Larsen; Capitán-Vallvey *et al* 1982).

nce the stretching frequency of the free NH group appears around 3400 cm⁻¹, the inution for DTDSA, as well as for other hydroxamic acids (Mathis 1961), can be tributed to the formation of hydrogen bonding. This point is also confirmed by erving the vibrational frequencies due to CO (1630 cm⁻¹); OH hydroxamic 0 cm⁻¹) and OH phenolic (3130 cm⁻¹). Indeed, the low frequency of these bands cate hydrogen bonding (Hadzi and Prevorsek 1957; Mathis 1961; Soler *et al* 1982). hus, it is concluded that the structural type (II) represents the most likely guration of DTDSA, in analogy with the proposed structure for salicylhydroxamic) and 5,5'-methylenedisalicyl-hydroxamic (MESA) acids (Larsen 1978; Capitán-vey *et al* 1982).

he absorption maxima of DTDSA and their molar absorptivities (ϵ) in aqueous and nolic solutions are given in table 1. A shoulder appears at 310 nm in both media. he absorption spectrum of DTDSA shows a remarkable pH dependence in aqueous



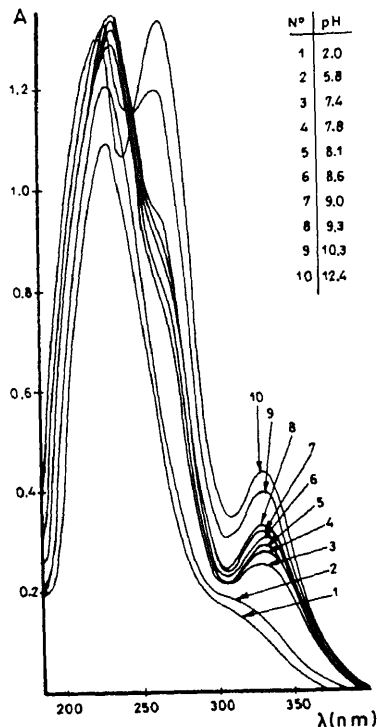


Figure 1. Variation of the absorption spectrum of DTDSA with pH. [DTDSA] = 2.5×10^{-5} M.

solution (figure 1). Thus, the absorption maximum at 220 nm experiment hypsochromic and hypochromic effects among 9.3 and 12.4 pH values. On the other hand, over pH 7.0, a new maximum appears at 330 nm, whose absorbances increase until pH = 10.8 ($\epsilon = 1.72 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$). Besides, above pH = 10.3, the absorption spectrum shows another maximum at 260 nm, which has a hyperchromic effect whose molar absorptivity is $5.32 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at pH = 11.2. Finally, two isobestic points appear at 280 and 303 nm. The former corresponding to solutions whose pH values are between 8.5–9.3; and the latter between 7.3–8.5. These effects are attributed to the dissociation steps.

Spectrophotometric measurements indicate that ethanolic solutions of DTDSA are stable for at least ten days, whereas their aqueous solutions, are stable for at least two months in acid and neutral media.

3.1b Solubility of DTDSA in water at different temperatures: The results obtained (table 2) indicate that the solubility of DTDSA increases linearly with temperature, in the investigated interval. At 25°C it is 0.156 g/l. Accordingly, the DTDSA is less soluble

Table 2. Solubility of DTDSA in water at different temperatures.

Temperature (°C)	20	30	40
Solubility (g/l)	0.146	0.167	0.180

Table 3. Dissociation constants of DTDSA in different media.

<i>pK</i>	Water			Ethanol-water (1:1)	
	Thamer	Schwarzembach	Chaberek-Martell	Schwarzembach	Irving-Rossotti
<i>pK</i> ₁		7.3	7.1	6.9	6.8
<i>pK</i> ₂	7.5	7.6	7.6	8.3	8.4
<i>pK</i> ₃	8.4	8.7	8.6	10.8	11.1
<i>pK</i> ₄		9.1	9.2	11.4	11.6

and Exner 1974; Deshpande and Jahagirdar 1977) it can be accepted that the oxamic acids are N-acids. Then, the *pK*₁ and *pK*₂ values of DTDSA can be assigned to the dissociation of the two NH groups and *pK*₃ and *pK*₄ values to the dissociation of phenolic groups. Similar assignments have been effected for SHA and MESHA (Deshpande and Jahagirdar 1977; Capitán-Vallvey *et al* 1982).

As was expected for OH groups (Irving and Rossotti 1956; Shukla and Tandon 1971; Deshpande and Kapoor 1977; Agrawal and Kharé 1977), the *pK*₃ and *pK*₄ values in alcoholic-aqueous medium are higher than those in aqueous solutions.

Chelating properties of DTDSA

Reactions of DTDSA with metal ions in aqueous medium: The complex-formation reactions of DTDSA with metal ions at different pH values, are described in table 4. The range over which the sensitivity was maximum for each metal ion and their detection limits (*pD*) are also shown in the same table.

Most of observed reactions are of precipitation. With Hg(II), Tl(III) and Ni(II), the precipitation takes place at pH ≤ 7. Coloured solutions were obtained only with Cu(II), Pd(II), Cr(III), and Cr(VI). W(VI) and Cr(VI) were found to react only in strongly acidic medium; Cr(III), Pb(II) and Th(IV) between pH = 4–6, and Y(III) in neutral medium.

Although 19 ions have *pD* values between 5 and 6, the sensitivity of reactions is generally not high. The ions whose reactions are the most sensitive are Zr(IV), Fe(II), Mn(II), Fe(III) and V(V).

The complex-formation reactions of DTDSA are comparable to those of other oxamic acids, such as phthalmonohydroxamic (FTMHA) (Estela 1981), isophthalaldihydroxamic (IFTDHA) (Jiménez 1982), dipicolindihydroxamic (DPDHA) (Forteza 1982), and especially SHA (Bhaduri and Ray 1952; Bhaduri 1956; Poddar *et al* 1966;

Table 4. Reactions of DTDSA with metallic ions and the effect of several masking agents of the metal-DTDSA reaction.

Metal-DTDSA reactions			Masking reactions ^b						
Used as	Colour of complex	Optimum pH range	pD^a	CN ⁻	F ⁻	Cit.	Ox.	NTA	EDTA
AgNO ₃	Light Yellow (pp)	4-6	3.9	- ^c	+	+	-	+	-
Pb(NO ₃) ₂	Light Yellow (pp)	4-6	4.3		+	+	+	-	+
Hg ₂ (NO ₃) ₂ · 2H ₂ O	Light Green-yellow (pp)	3-5	4.0		+	+	+	-	+
Hg(NO ₃) ₂ · H ₂ O	Light Green-yellow	7-9	4.5	-	+	+	+	-	-
Tl(NO ₃) ₃	Light Green-yellow	7-9	4.6	+	+	-	+	-	-
Bi(NO ₃) ₃ · 5H ₂ O	Yellow	>9	4.2	+	+	-	+	+	-
Cu(NO ₃) ₂ · 6H ₂ O	Green (pp)	7-9	5.5	+	+	+	+	+	+
Cd(NO ₃) ₂	Light Yellow (pp)	7-9	4.3	-	+	+	+	-	-
PdCl ₂	Orange	6-8	5.2	-	+	+	+	+	+
(NH ₄) ₆ Mo ₇ O ₂₄ · 4H ₂ O	Light Green-yellow	4-6	5.2	+	+	+	+	-	-
Fe(NO ₃) ₃ · 9H ₂ O	Red-violet (pp)	1-3	5.8		-	+	-	-	-
Fe(NH ₄) ₂ (SO ₄) ₂ · 5H ₂ O	Red-brown (pp)	1-3	6.0			+	+	+	+
Cr(NO ₃) ₃ · 9H ₂ O	Yellow	4-6	4.3	-	+	-	+	-	+
K ₂ CrO ₄	Orange	1-3	5.3		+	+	+	+	+
Co(NO ₃) ₂ · 6H ₂ O	Brown (pp)	7-9	5.5	+	+	+	+	+	+
Ni(NO ₃) ₂ · 6H ₂ O	Light Green-yellow	>9	4.6	-	+	+	+	+	+
Mn(NO ₃) ₂ · 6H ₂ O	Brown (pp)	7-9	5.5	+	+	+	+	+	+
NH ₄ VO ₃	Violet (pp)	1-3	5.8		+	+	+	+	+
UO ₂ (NO ₃) ₂ · 6H ₂ O	Orange (nn)	7-9	5.2	+	+	+	+	+	+

reacts with metal ions, through their orthohydroxyhydroxamic group and means of its dithio group.

Data on the influence of various masking agents on the complex-formation reaction with DTDSHA, in aqueous medium, are also summarized in table 4. With Th(IV), Hg(II), Cd(II), Fe(III), Cr(III) and Ca(II) the influence of the investigated masking agents is remarkable.

3.2b Extraction of the complexes: The observed colour reactions, after extraction of a benzene solution of Adogen 464, are given in table 5. Only 15 ions were found to be extracted indicating that the selectivity of DTDSHA can be improved by resorting to other extraction agents.

The sensitivities are of equal order, with pD values varying between 5 and 6; the most sensitive reactions being with Fe(II), Ti(IV), Fe(III) and V(V).

The extraction of hydroxamic acids complexes with inorganic ions has been reported (Agrawal 1980; Agrawal and Patel 1980) using organic solvents such as chloroform, ethylacetate, amyl and isoamyl alcohol, and 1-hexanol. Recent systematic studies have been published over the reactions of FTMHA (Estela 1981), (Jiménez 1982), and DPDHA (Forteza 1981) with metal ions, and their extraction from benzenic or toluenic solutions of the cationic resin Adogen 464. The colour reactions observed in these solutions and the pH range where they are produced, are in good agreement with those observed with DTDSHA.

3.2c Reactions of DTDSHA with metal ions over ion-exchange resins: Very sensitive assays have been reported (Fujimoto and Iwamoto 1963) to detect metal ions by their reaction with organic ligands after their absorption in some granules of the cationic ion-exchange resin. Similar studies were performed using DTDSHA for detection purposes after exchanging the metal ions in Dowex 1-X4 resin.

The results obtained are summarized in table 6. The data chart show considerable improvement in the sensitivity, the reaction with V(V) being more sensitive with a detection limit of 0.05 µg.

Table 5. Reactions of DTDSHA with metallic ions, after extraction with benzenic solution of Adogen 464.

Ion	Medium	Colour	pD
Bi(III)	NaOH	Yellow-orange	4.9
Cu(II)	NaOH	Green	5.4
Pd(II)	H ₂ O	Yellow-orange	5.0
Mo(VI)	HCl	Light green-yellow	5.2
Fe(III)	HCl	Red	5.9
Fe(II)	NaOH	Red	6.0
Co(II)	NH ₄ OH	Green	5.6
Ni(II)	NH ₄ OH	Green	5.2
Mn(II)	NH ₄ OH	Brown	5.5
V(V)	HCl	Violet	5.8
UO ₂ (II)	NH ₄ OH	Orange	5.3
Ti(IV)	HCl	Orange	6.0
W(VI)	HCl	Yellow-orange	5.4

Table 6. Reactions of DTDSA with metal ions over ion-exchange resins.

Ion	Colour	Detection limit (μg)
Cu(II)	Green	1.0
Pd(II)	Orange	0.5
Mo(VI)	Green	0.5
Fe(III)	Red	0.2
Cr(VI)	Red	2.0
V(V)	Violet	0.05
UO ₂ (II)	Orange	1.0
Ti(IV)	Orange	0.5

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Synthesis and characterization of phenolic oligomers

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Abstract. Phenolic oligomers were prepared by Friedel-Craft polymerization from different phenols with dichloro methane and 1,2-dichloroethane. The samples were characterized by IR spectra, viscosity measurement and thermal analysis by differential scanning calorimeter (DSC). The number average molecular weight ($\bar{M}_n$) was determined by vapour pressure osmometry (VPO) and by conductometric titration.

Keywords. Phenolic oligomers; *p*-cresol; differential scanning calorimeter (DSC); limiting viscosity number (LVN); vapour pressure osmometer (VPO).

1. Introduction

Friedel-Craft's (FC) reaction of benzene or substituted benzene with dichloromethane (DCM) and 1,2-dichloroethane (DCE) gives oligomers in which benzene nuclei are linked through methylene (Patel and Patel 1979) as well as ethylene bridges (Shinkle 1935; Towne 1937). Oligomers having methylene (Patel and Patel 1979) bridges and oligomers with ethylene (Patel *et al* 1979; Patel *et al* 1980) bridges, made from 8-hydroxy quinolines, salicylic acid and salicyldehyde under FC conditions have been reported. This paper reports the synthesis and characterization of different phenolic oligomers.

2. Experimental

2.1 Friedel-Craft polymerisation

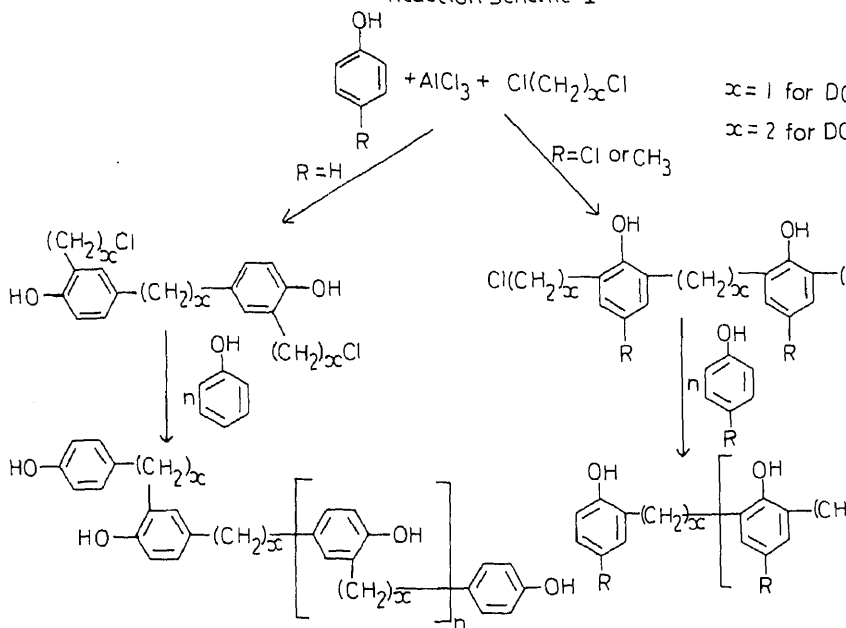
The chemicals used were of analytical grade. To phenolic compound (table 1) (0.20 mol) in a three-neck flask anhydrous aluminium chloride (1.00 mol for the DCM and 0.40 mol for the DCE oligomer) was added in powdered form. A condenser was fitted to the flask and ice cold water was circulated in the case of reaction with DCM. The entire assembly was placed in ice cold water. From the top of the condenser an aliquot of DCM (1.00 mol) or DCE (0.60 mol) was added. After the reactants were uniformly mixed, the temperature of the water bath was gradually increased upto 75°C for the reaction with DCM and 90°C for that with DCE. After the reaction was over, the temperature was maintained constant for 1.5 hours. The reaction mixture was kept overnight at room temperature. It was placed in ice bath and hydrochloric acid (50%) was added to the reaction product which was then filtered. It was washed with distilled water till free of the acid. The resin was further purified by dissolving in alkali (10% NaOH) and precipitated with acid (50% HCl). The resin was filtered, washed with distilled water till free of acid, and then dried. The general reaction is shown in reaction scheme 1.

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Table 1. Heat of fusion, molecular weight and limiting viscosity number oligomers.

Oligomers	Heat of fusion (ΔH_f) cal/mg by DSC	Molecular weight			Limiting viscosity number dl g ⁻¹ in methyl- ethylketone at 35°C
		$\bar{M}_n$ calculated	$\bar{M}_n$ VPO	$\bar{M}_n$ conductometry	
phenol-DCM	—	318	—	307	0.04
<i>p</i> -chlorophenol-DCM	10.81	843	802	786	—
2,4-dichlorophenol-DCM	0.80	352	383	332	—
<i>p</i> -cresol-DCM	2.67	360	399	397	0.05
α -naphthol-DCM	—	312	302	317	0.02
β -naphthol-DCM	—	312	369	343	0.03
phenol-DCE	—	360	342	399	0.02
<i>p</i> -chlorophenol-DCE	16.6	463	455	478	0.06
2,4-dichlorophenol-DCE	5.99	380	390	383	0.03
<i>p</i> -cresol-DCE	6.10	402	441	415	0.04
α -naphthol-DCE	—	342	—	361	—
β -naphthol-DCE	—	342	314	324	—

Reaction Scheme 1



estimating -OH groups in a chain. The limiting viscosity number measurements were carried out in MEK and pyridine solvents using an Ubbelohode suspended level type viscometer. A thermal study was also carried out. The heat of fusion, ΔH_f , was determined using a differential scanning calorimeter.

3. Results and discussion

All the oligomers were in powdered form and of dark-brown or reddish-brown colour. Most of them were soluble in common organic solvents. The IR spectra of the oligomers showed absorption bands in the region ascribed to C-H stretching vibration due to $-\text{CH}_2-$ ($2825\text{--}3000\text{ cm}^{-1}$) and $-\text{CH}_2-\text{CH}_2-$ ($2875\text{--}2950$) bridges. The bands due to $-\text{CH}_2-\text{CH}_2-$ are strong or medium as compared to $-\text{CH}_2-$ bridge. The distinct absorption bands at $1438, 1460, 1440, 1430\text{ cm}^{-1}$ represent methylene bending and scissoring modes which offer clear evidence for the existence of $-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-$ groups in these resins. This is further evident by the bands appearing in the region $1285\text{--}1355\text{ cm}^{-1}$ due to methylene bending (wagging and twisting) modes. The rocking of methylene groups in the polymer chain is exhibited in the region $750\text{--}850\text{ cm}^{-1}$. Absorption around 1300 cm^{-1} and 1250 cm^{-1} can be assigned to -OH deformation and C-O stretching vibrations respectively (Kozyrava and Malayu 1968). The bands observed at $1065, 1073, 1070, 1100\text{ cm}^{-1}$ etc. are assigned to ortho and orthopara substitution (Richard and Thompson 1947). A broad band between $3400\text{--}3260\text{ cm}^{-1}$ can be assigned to polymerically associated -OH group of phenolic oligomers.

The number average molecular weight ($\bar{M}_n$) of the phenolic oligomers obtained by vpo (James *et al* 1968) and conductometric titration (Chetterjee 1969) helps in the estimation of the degree of polymerization (DP) which was obtained by dividing the total amount of base added at short interval to neutralize all the -OH groups in the chain (Chetterjee 1970). For instance DP for *p*-chlorophenol-1,2-dichloro-ethane oligomers would be $652/210 = 3.1$. The product of the average degree of polymerization and repeating formula weight gave the $\bar{M}_n$ (3.1×154.5) = 479. The comparative study of vpo and conductometry data revealed (table 1) that $\bar{M}_n$ of the oligomers determined by both the techniques for both DCM- and DCE-systems agree fairly well.

In general it is revealed that limiting viscosity number (η), of the oligomers increased with increasing molecular mass. It is noted that the limiting viscosity number of the same oligomer sample was higher in pyridine than those in MEK (table 1). This indicates that pyridine is a good solvent. Industrially, viscosity measurement is useful in controlling (Marshall 1953; Dienes 1949) the flow of the polymer melt in polymer processing.

The data revealed that the heat of fusion, ΔH_f of DCM-oligomer was lower than that of corresponding DCE-oligomer. It is concluded that the methylene bridge has lowering effect on ΔH_f than the corresponding ethylene-bridge in the oligomers. Predominant endothermic peak is also observed in some cases. In such cases oligomers are softened below 350°C .

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Kinetics of nucleophilic substitution reactions of 1-chloromethylnaphthalene with anilines

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Abstract. Bimolecular rate constants have been estimated conductometrically for the reaction of 1-chloromethylnaphthalene (1-CMN) with aniline in four solvents to study solvent and temperature effects. The reaction of 1-CMN with various *m*- and *p*-substituted anilines has also been studied in methanol at three temperatures. The results have been analyzed with the help of various empirical relations.

Keywords. Hammett relation; Fairclough-Hinshelwood relation; iso-kinetic relation; Dimroth-Reichardt parameter.

1. Introduction

The kinetics of the nucleophilic substitution reactions of benzyl chloride have been studied very well (Radhakrishnamurti and Panigrahi 1970; Saksena and Bose 1975; Maccarone *et al* 1977). However, the kinetics of nucleophilic substitution reactions of 1-CMN have not been studied in a systematic manner. This prompted us to investigate the solvent, temperature and nucleophile effects on the kinetics of the nucleophilic substitution reactions of 1-CMN.

2. Experimental

2.1 Materials and methods

1-CMN was prepared by the method reported in the literature (Grumitt and Buck 1943). Solvents were purified by standard methods (Vogel 1978). Anilines were purified by either double distillation over zinc dust or by crystallization. Freshly purified solvents and reagents were used for each kinetic run. The uncertainty in the value of *k* is of the order of $\pm 2\%$.

2.2 Procedure

The reaction kinetics were followed by the conductometric method (Patel *et al* 1972). The reaction mixture of required concentration in a particular solvent was prepared by mixing thermostated solutions of 1-CMN (0.02 M) and the appropriate amine (0.04 M). The method of least squares was applied for calculating the rate constant and other parameters.

2.3 Product analysis

A solution of 0.2 M 1-CMN and 0.4 M aniline in 100 ml methanol was refluxed for 24 hours. The solvent was evaporated and the residue treated with anhydrous ether. The anilinehydrochloride which remained insoluble in ether was then removed and the ether was evaporated. The residue remaining after removal of ether was chromatographed over silica gel using benzene as eluent. The solid product 1-naphthyl 1-methyl-2-pyrrolidone aniline (yield 90 %, m.p. 65°C) was characterized by IR and elemental analysis.

3. Results and discussion

3.1 Effect of nucleophile

For the reaction of 1-CMN with anilines the values of second order rate constant, activation energy E_a , Arrhenius frequency factor $\log A$, free energy of activation $\Delta G^\ddagger$, enthalpy of activation $\Delta H^\ddagger$ and entropy of activation $\Delta S^\ddagger$ are listed in table I.

Electron-releasing substituents (-OMe, -OEt, -Me) accelerate the reaction while electron-withdrawing substituents (-Cl, -NO₂) retard the reaction.

The Hammett plot was found to be linear at all temperatures. The relation worked out at 35°C as:

$$\log k_2 = (-0.737)\sigma - 3.541,$$

where σ is the substitution constant. The correlation coefficient was estimated to be about 98 % at all temperatures. The values of reaction constant, ρ , were found to be -0.737, -0.707 and -0.639 at 35, 40 and 45°C respectively. The value of ρ becomes more negative with decrease in temperature. This indicates that the sensitivity of the reaction with anilines to the substituent effect increases with decrease in temperature.

The iso-kinetic relation was worked out at 35°C as:

$$\Delta H^\ddagger = (383.7)\Delta S^\ddagger + 24.51,$$

with correlation coefficient equal to 99.2 %. The isokinetic temperature $\beta = 383.7$ K. The applicability of this relationship shows that each reaction in the present study follows the same mechanism *i.e.* S_N2 (Leffler 1955).

The Fairclough-Hinshelwood relation (Fairclough and Hinshelwood 1953) was found to be linear. The relation was worked out as:

$$\log A = (-93.12)[1/(E_a)^{1/2}] + 31.19$$

$$(\text{correlation coefficient} = 98.8 \%).$$

This indicates that Arrhenius factor A and energy of activation E_a are not independent but linearly related and the present reaction is bimolecular process.

The Bronsted relationship was studied at 35°C. The linear relation was worked out as:

$$\log k_2 = (0.195)pK_a - 4.406$$

with correlation coefficient is equal to 98 %.

3.2 Medium effect

The second order rate constant for the reaction of 1-CMN with aniline in different solvents is given in table II.

Table 1. Effect of nucleophile on the rate of reaction in methanol.

Anilines pK_a (H ₂ O 35°C)	$k_2 \times 10^4$ (l. mole ⁻¹ sec ⁻¹)			E_a Kcal. mole ⁻¹ (KJ. mole ⁻¹) (± 0.5)	$\Delta G^\ddagger$ (35°) ± 0.02 Kcal. mole ⁻¹ (± 0.084 KJ. mole ⁻¹)	$\Delta H^\ddagger$ (35°) ± 0.8 Kcal. mole ⁻¹ (± 3.35 KJ. mole ⁻¹)	$\Delta S^\ddagger$ (35°) ± 2.2 cal.deg. ⁻¹ mole ⁻¹
	35°	40°	45°				
p -OMe (5.16)	5.611	9.079	13.768	17.41 (72.87)	22.63 (94.68)	16.81 (70.33)	-18.89
p -OEt (5.05)	5.049	8.211	11.940	16.62 (69.53)	22.70 (94.98)	16.02 (67.03)	-21.65
p -Me (4.90)	3.266	5.173	7.973	16.78 (70.21)	22.96 (96.07)	16.17 (67.66)	-22.01
H (4.45)	2.464	3.724	6.095	17.62 (73.72)	23.14 (96.82)	17.01 (71.17)	-19.92
p -Cl (3.83)	1.715	2.777	4.525	18.73 (78.36)	23.35 (97.70)	18.12 (75.81)	-16.99
m -Cl (3.39)	1.461	2.344	3.814	18.47 (77.28)	23.45 (98.12)	17.87 (74.77)	-18.14
m -NO ₂ (2.35)	0.912	1.578	2.796	21.65 (90.58)	23.74 (99.33)	21.04 (88.03)	-8.78
p -NO ₂ (0.93)	0.839	1.433	2.533	21.25 (88.91)	23.79 (99.54)	20.65 (86.40)	-10.22

Table 2. Medium effect on the rate of reaction.

Solvent (dielectric constant, ϵ)	$k_2 \times 10^4 \text{ lit. mole}^{-1} \text{ sec}^{-1}$				$\Delta H^\ddagger$ (35°) $\pm 0.46 \text{ Kcal.}$ mole^{-1} ($\pm 1.95 \text{ KJ.}$ mole^{-1})	$\Delta G^\ddagger$ (35°) $\pm 0.02 \text{ Kcal.}$ mole^{-1} ($\pm 0.08 \text{ KJ.}$ mole^{-1})	$\Delta S^\ddagger$ (35°) $\pm 2.0 \text{ Cal.}$ mole^{-1} deg^{-1}
	30°	35°	40°	45°	50°		
Methanol (32.6)	1.618	2.464	3.724	6.098	8.610	23.14 (96.82)	-23.44
Ethanol (24.3)	1.059	1.611	2.512	3.917	5.546	23.39 (97.86)	-24.84
Isopropanol (18.3)	2.187	3.111	4.842	7.430	10.789	15.17 (63.47)	-25.28
<i>n</i> -butanol (17.1)	0.816	1.142	1.967	3.126	4.456	23.60 (88.74)	-22.97
<i>t</i> -butanol (12.2)	—	8.261	—	—	—	—	—

Solvolysis rate $k_1 \times 10^6 \text{ sec}^{-1}$, methanol 3.02; isopropanol 4.21.

found to be extremely negligible compared to S_N2 reaction rates (solvolysis rate for methanol and isopropanol are mentioned in the footnote of table 2). Therefore the effect of solvolysis on bimolecular rates can be ignored.

The rate constant of the reaction decreased with the decrease in dielectric constant (ϵ) of the solvent *i.e.* the rate of reaction decreases from methanol to ethanol to *n*-butanol but the rate constant of the reaction in iso-propanol does not fit in this trend. The unusual behaviour observed in isopropanol could be due to the steric effect. In isopropanol, due to the bulk of the solvent reactants, and more particularly anilines, are expected to be very poorly solvated. This probably makes the reagents more reactive and hence the higher rate in isopropanol. This was further supported by studying the same reaction in *t*-butanol *i.e.* the rate of reaction was found to be higher than in isopropanol even though the polarity of *t*-butanol is lower. For the reactions of 1 and 2 naphthacyl bromides with a variety of nucleophiles in aliphatic alcohols similar higher rates in case of isopropanol have been observed (Patel 1982).

The relations between rate constant and some dielectric constant functions like $\log \epsilon$, $\epsilon - 1/2 \epsilon + 1$ (Kirkwood's function) and $1/\epsilon$, were found to be curvilinear (which are not shown here). These are the bulk or macroscopic properties of the medium and do not truly represent the effect of solvent polarity on reaction rates.

The relation between rate constant and Dimroth-Reichardt's, E_T (Reichardt 1965), parameter was found to be linear (the rate constant in isopropanol was not considered due to its unique behaviour). The linear relation was worked out at 50°C as:

$$\log k_2 = (0.0538) E_T - 6.051$$

(correlation coefficient = 99.3 %)

3.3 Temperature effect

For each reaction the plot of $\log k_2$ against $1/T$ was found to be linear. This shows that each reaction exhibits Arrhenius dependence. The values of energy of activation (E_a) free energy of activation ($\Delta G^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$) and entropy of activation ($\Delta S^\ddagger$) listed in tables 1 and 2 are of the same order, observed for other bimolecular nucleophilic substitution reactions. The values of $\Delta G^\ddagger$ are in accordance with the relation given by absolute rate theory ($k = RT/Nh \exp -\Delta G^\ddagger/RT$) *i.e.* $\Delta G^\ddagger$ decreases with increase in k_2 . $\Delta S^\ddagger$ is found to be negative as expected for the bimolecular reaction taking place in solution.

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Structural and catalytic studies of promoted iron oxide catalysts used in the dehydrogenation of ethylbenzene to styrene

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Abstract. Alkali-ion promoted iron oxide was used as a catalyst for the non-oxidative dehydrogenation of ethylbenzene to styrene. Catalytic performance studies showed high activity, with selectivity $\approx 93\%$ and conversion $\approx 49\%$. The fresh and used catalysts were characterised by various physicochemical techniques like scanning electron microscopy, x-ray diffraction and Mössbauer spectroscopy. X-ray and Mössbauer data clearly show the presence of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 in the used catalysts and $\alpha\text{-Fe}_2\text{O}_3$ in the fresh catalyst, the phases being identified from their standard d values and hyperfine interaction parameters.

Keywords. Promoted iron oxide catalysts; ethylbenzene dehydrogenation; Mössbauer studies.

1. Introduction

Styrene is produced commercially by the catalytic dehydrogenation of ethylbenzene in the vapour phase. This is an endothermic reaction effected by an equilibrium which favours the products as the temperature is increased and the pressure reduced. Superheated steam is used to provide heat needed for the reaction, to reduce the ethylbenzene and hydrogen partial pressures for maximising yields, and to keep the catalyst clean and active (Kaeding 1973; Sittig 1978).

Alkali promoted iron oxide is known to be distinctly better than any other catalyst with an activity over an order of magnitude higher than the unpromoted oxide and is favoured in the industrial process for ethylbenzene conversion (Lee 1973; Scheeline 1977; Courty and Le Page 1979). Although several catalytic performance studies have been carried out, there is a dearth of physicochemical characterisation studies for these catalysts leading to explanations regarding active species and catalytic performance.

In this study, we report the preparation, structural characterisation and catalytic performance of a potassia promoted, chromia stabilised iron oxide catalyst similar to the commercial catalyst Shell 105. The structural changes occurring during the catalytic conversion have been investigated by x-ray diffraction (XRD), Scanning electron microscopy (SEM) and Fe^{57} Mössbauer spectroscopy. Our results clearly indicate the formation of a spinel phase, namely Fe_3O_4 during the reaction. Other complex phases like FeCr_2O_4 , $\text{K}_2\text{Fe}_{22}\text{O}_{34}$, etc. were not observed.

2. Experimental

2.1 Catalyst preparation

The $\alpha\text{-Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3 + \text{K}_2\text{O}$ catalyst was prepared by the coprecipitation technique. Iron hydroxide was first precipitated from a solution of iron nitrate by the addition of NH_4OH . The resultant precipitate was partially dried and soluble salts of potassium carbonate and potassium dichromate were added. The slurry was washed, dried, finely ground and then transformed into 5 mm diameter pellets. The product was calcined at 700°C in air for 3 hours. Quantitative chemical analysis of the catalyst gave the following composition: Fe_2O_3 (88.4 wt %) K_2O (8.9 wt %) Cr_2O_3 (1.7 wt %).

2.2 Catalyst characterisation and reaction procedure

Pellets of freshly calcined and used catalysts were finely powdered and characterised by XRD, SEM and Fe^{57} Mössbauer spectroscopy. XRD patterns were recorded on a Philips PW 1730 x-ray diffractometer using $\text{CuK}\alpha$ -radiation with a nickel filter ($\lambda = 1.54 \text{ \AA}$). Scanning electron micrographs were recorded on a Cambridge stereoscan 150 microscope. Mössbauer spectra were recorded with a conventional constant acceleration electromechanical drive coupled to a nuclear data (model no. ND 100) multichannel analyser operating in the time mode. A 25 mCi $^{57}\text{Co}:\text{Rh}$ source was used to record the spectra at room temperature. A metallic iron foil (25μ) was used to calibrate the spectrometer and all isomer shifts were measured with respect to that of metallic iron. Hyperfine interaction parameters were computed using an iterative, non-linear least square MOSFIT program on an ICL 1409S computer.

The continuous flow dehydrogenation reaction was carried out on a fixed bed reactor at atmospheric pressure. Five grams of the catalyst in the form of pellets were packed into the metallic reactor placed in an electrically heated tubular furnace. Temperature was maintained within an accuracy of $\pm 5^\circ\text{C}$ by an on-off type temperature controller using a calibrated chromel-alumel thermocouple kept at the center of the catalyst bed.

Catalytic runs were carried out under fixed reaction conditions (table 1). The organic effluents were collected at regular intervals and analysed by gas chromatography. A 2 m column packed with 5% diisodecyl phthalate and Bentone-34 was used for the analysis at 373 K.

Table 1. Catalytic performance data for the dehydrogenation reaction.

Experimental conditions:

Feed: $\text{EB}:\text{H}_2\text{O} = 1:2.25$ mole

Temperature: 883 K

*W.H.S.V. in hr^{-1} : 0.7

Conversion of EB in mole %: 49

Selectivity to styrene in mole %: 93

Product distribution in weight %:

Benzene = 1

Toluene = 1.6

Ethylbenzene (EB) = 63.6

Styrene = 34.0

3.1 Catalytic activity

The non-oxidative dehydrogenation of ethylbenzene over iron-oxide catalysts gives styrene as the major product and small amounts of benzene and toluene as by-products.

The main reaction can be expressed as:



Potassium carbonate and chromium oxide are incorporated into the catalyst as the promoter and the stabiliser respectively. Lee (1973) has proposed that the potassium promoter operates specifically at the surface of the catalyst and increases the catalytic activity by promoting electron transfer at the solid-gas interface. Catalytic performances under fixed experimental conditions were evaluated as follows:

Ethylbenzene (EB) conversion, C (% mole)

$$= (\text{EB}_{\text{inlet}} - \text{EB}_{\text{outlet}} / \text{EB}_{\text{inlet}}) \times 100 \quad (2)$$

Product selectivity, Si (% mole)

$$= (\text{Product } (i) / \text{EB}_{\text{inlet}} - \text{EB}_{\text{outlet}}) \times 100 \quad (3)$$

Product yield, Yi (% mole)

$$= (\text{Product } (i) / \text{EB}_{\text{inlet}}) \times 100 \quad (4)$$

with yield = conversion $\times$ selectivity for a given product.

Table 1 gives the catalytic performance results of a typical run carried out for twenty hours. A high selectivity to styrene $\approx 93\%$ with EB conversions $\approx 49\%$ was observed. Yields of toluene were larger than benzene as observed for commercial catalysts (Wang *et al* 1983; Lee 1973). Catalytic activity was tested over an extended period ≈ 80 hrs. Figure 1 shows schematically the catalytic performance as a function of time on stream during two runs. The selectivity to styrene increases rapidly to 93% within the first few hours and remains steady with time on stream for both runs.

Percentage yields of side products toluene and benzene were low $1-2\%$. Lower yields of toluene and benzene during the first run are attributed to the increased coking rate caused by the increased EB feed. Coking decreases the acidic centres and dealkylation which takes place at Bronsted acid centres also decreases (Kulkarni and Kulkarni 1983).

Since the selectivity to styrene was found to be very high in these catalytic runs, physicochemical characterisation of these catalysts was undertaken using various techniques like XRD, SEM and Fe^{57} Mössbauer spectroscopy. These techniques have provided valuable information about the crystallite sizes and distribution of different phases formed during conversion.

3.2 X-ray diffraction studies

From a systematic analysis of the d values of the observed x-ray peaks with the help of standard ASTM data, it is possible to identify the pattern as due to the single phase of $\alpha\text{-Fe}_2\text{O}_3$ in fresh catalyst.

Crystallite sizes were calculated from x-ray line broadening using the Scherrer equation

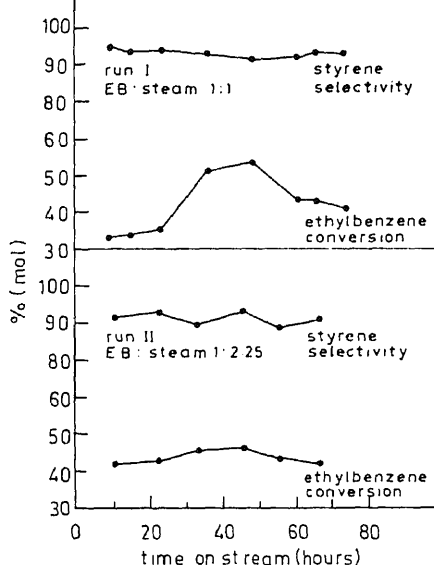


Figure 1. Selectivity to styrene and ethylbenzene conversion over iron oxide catalysts for run I (EB to steam ratio = 1:1) and run II (EB to steam ratio = 1:2.25) with time on stream.

where $\lambda = 1.543 \text{ \AA}$, θ is the Bragg angle and β the pure diffraction broadening (Klug and Alexander 1974). The fresh catalyst showed a distribution of crystallite sizes, 355 Å, 883 Å and 1025 Å, determined from the major reflections (104), (024) and (110) of the $\alpha\text{-Fe}_2\text{O}_3$ structure.

An x-ray diffractogram of the used catalyst was analysed in a similar fashion. From a comparison with ASTM data it was easy to assign patterns to Fe_3O_4 and K_2CrO_4 as major phases. Traces of $\alpha\text{-Fe}_2\text{O}_3$ are also present. The lattice parameter for Fe_3O_4 ($a_0 = 8.38 \text{ \AA}$) was close to that of bulk magnetite ($a_0 = 8.376 \text{ \AA}$). The average crystallite size from x-ray line broadening was 378 Å determined from the intense (220), (311) and (400) reflections of the Fe_3O_4 structure. Crystallite sizes were found to be more uniform after the catalytic dehydrogenation reaction.

The xrd-patterns did not show the presence of FeCr_2O_4 and $\text{K}_2\text{Fe}_{22}\text{O}_{34}$ phases, previously observed in iron oxide catalysts (Shibata and Kiyoura 1969; Courty and Marcilly 1983). However, minute quantities of these compounds may be present below the xrd detection limit.

SEM photographs of the fresh and used catalyst pellets showed the presence of large particles with sizes ranging from 5000–20,000 Å. The fresh catalyst had well-defined particles. In the used catalyst, small clusters were deposited on the large particles and their formation may be attributed to reduction of the catalyst. Particle sizes for the fresh and used catalyst do not change. Courty and LePage (1979) have attributed increased selectivity for dehydrogenation of ethylbenzene to large particle sizes ($\approx 5000 \text{ \AA}$).

3.3 Fe^{57} Mössbauer spectroscopic analysis

Table 2. Hyperfine interaction parameters derived from room temperature Mössbauer spectra for fresh and used catalysts.

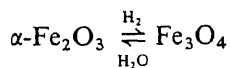
Mössbauer parameters	Fresh catalyst $\alpha\text{-Fe}_2\text{O}_3$	Used catalyst		
		$\alpha\text{-Fe}_2\text{O}_3$	Fe_3O_4^A	Fe_3O_4^B
I.S. (± 0.02 mm/sec)	0.43	0.31	0.29	0.69
ΔE_Q (± 0.05 mm/sec)	0.20	0.15	-0.01	0.05
H_n/KOe (± 5 KOe)	515	510	497	459
Line width (± 0.05 mm/sec)	0.39	0.60	0.60	0.73

I.S. $\equiv$ Isomer or chemical shift (δ); $\Delta E_Q \equiv$ Quadrupole splitting; $H_n \equiv$ Hyperfine field in Kilo oersteds (KOe). ^{A,B} Tetrahedral or Octahedral sites.

temperature values, the six line pattern was assigned to Fe^{3+} ions in $\alpha\text{-Fe}_2\text{O}_3$ (Greenwood and Gibb 1971). This result agrees well with the XRD data.

After a careful analysis of the broad experimental spectrum of the used catalyst after hours of dehydrogenation, three sextets were resolved. The derived hyperfine parameters given in table 2 are characteristic of Fe^{3+} in $\alpha\text{-Fe}_2\text{O}_3$, Fe^{3+} (A) and $\text{Fe}^{3+}/\text{Fe}^{2+}$ (B) in Fe_3O_4 (MEDI 1974). The parameters show an excellent agreement with corresponding values reported in the literature for pure phases (Kundig and Argrove 1969). The ratio of $\alpha\text{-Fe}_2\text{O}_3$: Fe_3O_4 was found to be 0.03, indicating that a large amount of $\alpha\text{-Fe}_2\text{O}_3$ was reduced to Fe_3O_4 during the reaction. Because of the high sensitivity and resolution of the Mössbauer spectroscopic technique, it was possible to identify the $\alpha\text{-Fe}_2\text{O}_3$ phase even in the presence of a large amount of Fe_3O_4 . However no interaction of the promoter (K_2O) and stabiliser (Cr_2O_3) with the main active agent $\alpha\text{-Fe}_2\text{O}_3$ was observed. The fresh and used catalysts have been studied by conversion electron Mössbauer spectroscopy to identify additional species, if any, present on the surface. In addition to the bulk species, namely $\alpha\text{-Fe}_2\text{O}_3$ (fresh catalyst) and $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 (used catalyst), a small concentration of new surface species $\alpha\text{-FeOOH}$ (used catalyst) have been identified through their characteristic hyperfine interaction parameters ($\delta = 0.321$ mm/sec, $\Delta E_Q = 0.036$ mm/sec, $H_n = 376$ KOe) (Tricker *et al* 1982).

From the characterisation studies using bulk techniques, partial reduction of Fe_2O_3 to Fe_3O_4 , but no subsequent reduction to metallic iron, was observed. The rate of reduction to Fe_3O_4 is lowered by steam (Viswanath *et al* 1975). Because of the simultaneous presence of hydrogen and steam a steady state is established between the two phases.



Since the reduction of $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 is rapid, the steady state (composed of a mixture of $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$) is attained after a few hours under operating conditions. The active interface, with a distribution of acidic-basic sites is one of the factors responsible

P_{H_2O}/P_{H_2} value and the large amount of lattice disorder (Pernicone and Traina 1979). Distribution of Cr^{3+} in the catalyst also delays the α - Fe_2O_3 reduction (Kung et al 1981). However chromia concentration in the catalyst is too low to have a significant effect.

4. Conclusion

In summary, it is seen that the α - Fe_2O_3 - Cr_2O_3 - K_2O catalyst has exhibited very high activity/selectivity over an extended period of time. Physicochemical characterisation has identified the changes occurring during the catalytic reaction i.e. the partial reduction of α - Fe_2O_3 to Fe_3O_4 and stabilisation of these two phases in the bulk.

Acknowledgements

The authors thank Dr P Ratnasamy and Dr A P B Sinha for many useful discussions and INSA, New Delhi for partial support. One of us (BS) thanks INSA for a fellowship.

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Surface characterisation of an iron oxide catalyst ethylbenzene $\rightarrow$ styrene): An XPS study

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Abstract. Surface chemistry and structural changes of a potassia promoted, chromia stabilised iron oxide catalyst were examined before and after the non oxidative dehydrogenation of ethylbenzene to styrene using x-ray photoelectron spectroscopy (xps).

xps binding energies of the Fe(2p, 3s, 3p, 3d), K (2p, 3s, 3p), Cr(2p, 3s, 3p) and O(1s) levels along with characteristic shifts in the binding energies, spin-orbit splittings and satellite, multiplet splittings help in identifying surface active species such as Fe₂O₃, Fe₃O₄, FeOOH at the surface of fresh and used catalysts.

Introduction

In an earlier paper (Sayyed *et al* 1985), we have reported the catalytic performance (conversion and selectivity) results on dehydrogenation of ethylbenzene to styrene over potassia promoted iron oxide catalyst. The catalyst was characterised by x-ray diffraction, scanning electron microscopy and Fe⁵⁷ Mössbauer spectroscopy (transmission and conversion modes).

Since catalytic reactions basically occur at the surface, the same catalyst has also been studied using a modern surface analytical tool, namely x-ray photoelectron spectroscopy (xps) to understand the electronic structure of surface active species and the catalytic reaction.

In this paper we report the xps experimental results and its analysis. The surface active species such as Fe₂O₃, Fe₃O₄, FeOOH were identified through the characteristic shifts in their binding energies, spin-orbit splittings, satellite and multiplet structures. All these results are evaluated in comparison with the bulk experimental data to speculate on the mechanistic aspects of the catalytic reaction.

Experimental

x-ray photoelectron spectra of the fresh and used catalysts were recorded at room temperature on a VG scientific ESCA 3 MK II spectrometer. MgK_α (1253.6 eV) radiation was used for excitation. The catalyst sample was mounted on a suitable holder and photoelectron spectra were recorded for the as-received, etched (using argon ion bombardment), fractured and powdered pellets. Binding energies (BE) were determined

using the C(1s) level as reference (285.0 eV). Photoelectron spectra of standard compounds like KCl, K_2CrO_4 , KNO_3 , $\alpha-Fe_2O_3$, Fe_3O_4 , $FeCr_2O_4$, Cr_2O_3 etc. were also recorded for standardisation and identification of the surface species.

3. Results

X-ray photoelectron spectra of Fe(2p, 3s, 3p, 3d), O(1s), K(2p, 3s, 3p) and Cr(2p, 3s, 3p) levels of the fresh and used catalysts were scanned at room temperature. Tables 1 and 2 summarise the BE values of fresh and used catalysts for the respective levels of different constituents.

Table 1. Binding energy values of the Fe(2p, 3s, 3p), K(2p), O(1s) levels in eV from xps spectra of the fresh catalyst.

Sample	Fe					K		O
	$3p_{1/2}$	3s	3s multiplet structure	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	1s
As-received	55.6	93.2	100.1	710.5	724.6	292.7	295.6	529.5 531.7
Etched (I) with argon ions	55.1	93.1	99.7	710.5	723.6	292.6	296.0	529.9 531.8
Etched (II) with argon ions	55.3	93.3	100.2	710.5	723.6	292.7	295.7	529.8 531.7
Powdered	55.5	93.3	99.9	710.6	723.6	292.8	295.6	529.5 531.7

Table 2. Binding energy values of the Fe(2p, 3s, 3p), K(2p), Cr(2p), O(1s) and CL(2p) levels in eV from XPS spectra of the used catalysts.

Sample	Fe					K		Cr	O	CL
	$3p_{1/2}$	3s	3s multiplet structure	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	2p	1s	2p
As-received	56.3	94.5	102.7	711.6	725.1	293.4	296.2		530.8	199.0 200.8
Etched (I) with Ar ions	54.6	92.7	98.3 102.6	709.9	723.0	294.0	296.6	576.3	529.6 531.6	199.0 201.4
Etched (II) with Ar ions	54.8	92.7	98.3 102.2	709.9	723.2	294.1	296.7	576.6	529.6 531.6	199.7 201.0
Fractured	55.1	93.0	98.8 102.8	709.9	723.2	292.8	296.5	576.9	530.1	nil
Powdered	55.8	93.4	99.2	710.3	724.3	292.7	295.7	576.8	530.4	nil

3.1 Fresh catalyst

In the high resolution scan of the Fe(2p) region, Fe(2p_{1/2}) and (2p_{3/2}) levels were detected at BE 723.9 eV and 710.5 eV respectively. The spin orbit splitting of the 2p bands ($\Delta E_{2p} = E_{2p_{1/2}} - E_{2p_{3/2}}$) is ≈ 14.1 eV. A 2p_{3/2} shake-up satellite (ss) is detected at BE 718.5 eV corresponding to an energy separation $\Delta E_{ss} \approx 8.0$ eV. These binding energies, together with the broad satellite are characteristic of an Fe³⁺ species (Brundle *et al* 1977; Rao *et al* 1979; Kurtz and Henrich 1983).

The Fe(3s) level at BE 93.2 eV has a multiplet structure at BE ≈ 100.1 eV. The magnitude of multiplet splitting for 3s core level holes for various iron compounds has been observed to be as large as 7.0 eV, but is smaller for levels having different principal quantum numbers (Carver *et al* 1972). These values are characteristic of high spin ferric species in compounds like Fe₂O₃, FeCl₃ etc. (Carver *et al* 1972; Rao *et al* 1979). We have used both Fe(2p) shake-up satellites and Fe(3s) multiplet splitting in our identification of the surface iron species (Carlson 1975; Frost *et al* 1974; Okamoto *et al* 1975). The Fe(2p, 3s) peak positions do not show appreciable change in the BE values after repeated etching with argon ions or when the as-received pellets are fractured and powdered.

A broad asymmetric O(1s) band is recorded in the high resolution scan of the fresh catalyst. From the spectrum, O(1s) peak at 529.8 eV is easily distinguishable from a weak shoulder around 531.7 eV. These BE are typical of oxide and hydroxyl species (Brundle *et al* 1977) and the latter persists after etching and powdering.

The observed peaks at BE 292.8 eV and 295.6 eV are due to the K(2p_{3/2}) and K(2p_{1/2}) levels respectively and lie in the range of K(2p) BE values. The potassium species were assigned to K₂O, which has been added as a promoter. Cr (2p, 3s, 3p) bands were not clearly observed at the surface of the fresh catalyst.

3.2 Used catalyst

For the used catalyst, the as-received, etched and powdered samples give x-ray photoelectron spectra with characteristic differences as discussed below.

The high resolution scan in the Fe(2p) region for the used, as-received, catalyst gave Fe(2p_{3/2}, 2p_{1/2}) bands centred at BE 711.6 eV and 725.1 eV respectively. The energy separation, ΔE_{2p} was ≈ 13.5 eV. Fe(2p) satellite structure was not detected. The BE values are characteristic of high spin Fe³⁺ ions (Brundle *et al* 1977). X-ray photoelectron spectra observed for etched, fractured and powdered samples in the Fe(2p) region were similar. The Fe(2p_{3/2}, 2p_{1/2}) levels were centred at lower BE 709.9 eV and 723.0 eV respectively with Fe(2p) spin orbit splitting 0.4 eV less than that of as-received catalyst. This value is known to decrease slightly with lower oxidation state (Rao *et al* 1979). The broad Fe(2p_{3/2}) band has a shoulder on the lower BE side. The main peak is assigned to the Fe³⁺ state and the shoulder to Fe²⁺ state (Brundle *et al* 1977; Rao *et al* 1979; Asami *et al* 1976). A Fe(2p_{3/2}) shake-up satellite is also detected at BE 715.8 eV giving a characteristic Fe²⁺ exchange splitting ≈ 5.9 eV. The Fe(2p_{1/2}) peak is also broad and asymmetric indicating the presence of a shoulder at lower BE.

The Fe(3s) band (BE 94.5 eV) at the surface of as-received used catalyst has a multiplet structure with splitting ≈ 8.2 eV, characteristic of high spin Fe³⁺ ions. The high intensity of the multiplet structure compared to the main 3s band may be due to an additional contribution from some impurity (perhaps Si) present in the reactor. The

spin iron compounds. For the etched, fractured and powdered catalysts, the $O(1s)$ band centred around 529.7 eV is broad and asymmetric indicating a superposition of two peaks with close BE values. In addition to the $Fe(3s)$ multiplet structure at BE 102.6 eV characteristic of Fe^{3+} species, another multiplet structure is observed at BE 98.3 eV. This may be assigned to the Fe^{2+} species (Rao *et al* 1979; Carver *et al* 1972). These BE and multiplet splitting values are characteristic of high spin Fe^{2+}/Fe^{3+} species.

A broad asymmetric band at ≈ 200 eV detected at the surface of as-received and etched catalysts could be resolved into two peaks at BE 199.3 eV and 200.8 eV respectively. These values are close to the $Cl(2p_{3/2}, 2p_{1/2})$ BE values and may be assigned to chlorine present as an impurity at the surface. They vanish on fracturing and powdering of the used catalyst and are not observed after subsequent catalytic reactions.

The band at 530.8 eV at the surface of the as-received catalyst corresponding to the $O(1s)$ band is assigned to an oxide species (Brundle *et al* 1977). After etching the sample, a broad asymmetric $O(1s)$ band was observed which could be resolved into two peaks at BE 529.6 eV and 531.6 eV. These bands can be assigned to usual oxide and surface defect oxide or hydroxyl species. On fracturing and powdering the catalyst, the $O(1s)$ band (BE 530.1 eV) regains its own symmetry and may be assigned to the predominant oxide species.

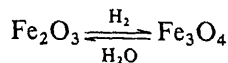
The $K(2p_{3/2})$ and $K(2p_{1/2})$ levels for as-received and etched catalysts were at BE about 0.8 to 1 eV higher than that of the fresh catalyst. For the fractured and powdered catalyst surface, these BE values equalled those of the fresh catalyst.

Both sets of binding energies lie within the range of $K(2p)$ BE values and may be assigned to KCl or K_2O . $Cr(2p_{3/2})$ bands at the surface of etched, fractured and powdered catalysts were centred at BE 576.7 eV whereas $Cr(3p, 3s, 2p_{1/2})$ levels were very weak. The BE agree with those reported in literature for Cr^{3+} species and may be assigned to Cr_2O_3 (Rao *et al* 1979).

4. Discussion

The high spin ferric species at the surface of the fresh catalyst is assigned to Fe_2O_3 taking into consideration the close agreement of the $Fe(2p, 3s)$ binding energies, spin-orbit and multiplet splittings and conversion electron Mössbauer spectroscopic (CEMS) results reported earlier (Sayyed *et al* 1985). The surface composition is nearly identical with that of the bulk catalyst.

For the used catalyst, CEMS spectra have indicated the presence of $\alpha\text{-Fe}_2O_3$, Fe_3O_4 and $\alpha\text{-FeOOH}$. The Fe^{2+}/Fe^{3+} high spin species, identified from xps data at the surface of etched, fractured and powdered catalyst are attributed to the two oxidation states of iron in Fe_3O_4 (Rao *et al* 1979). Since the octahedrally coordinated Fe^{3+} species is not easily distinguishable from the tetrahedrally coordinated Fe^{3+} species (Brundle *et al* 1977), the observed asymmetry in spectra is due to the superposition of the peaks of Fe_2O_3 and $FeOOH$ as well. The formation of the $FeOOH$ phase is due to steam. The chemical reaction can be expressed as



This reduction seems to be necessary for the catalytic reaction of CO and H_2 to CH_4 and H_2O .

occurring at the surface. As a function of time, the equilibrium between Fe_2O_3 and Fe_3O_4 is established from the surface into the bulk. This thermodynamic balance is possible for the high selectivity and conversion. Any disturbance of this equilibrium results in a drop in catalytic performance parameters.

Knowledgegement

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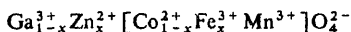
Mössbauer effect studies of the $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ system

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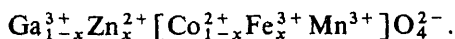
Abstract. Mössbauer studies have been carried out on the spinel system $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ at room temperature (294 K) for the values of $X = 0, 20, 40, 50, 60, 80$ and 100 (where X denotes the mole percent of ZnFeMnO_4 in GaCoMnO_4). All the compounds showed well resolved quadrupole split doublets. Isomer shift values varied between 0.26 and 0.48 mm/sec. The value of quadrupole splitting increased with increasing u parameter. The increase in u parameter is attributed to the replacement of Ga^{3+} by Zn^{2+} ions at the A-site. From Mössbauer studies, the ionic configuration of the system is suggested as



Keywords. Spinel; isomer shift; quadrupole doublet; u parameter.

Introduction

One of the most exciting areas of the Mössbauer studies is the detailed study of spinel systems by changing the composition of solid solution in a controlled and continuous manner, alongwith the other experimental methods available. Literature survey (Vatzky *et al* 1969; Mathur *et al* 1967; Jain and Darshane 1983) revealed that many workers have reported the ionic configuration of ferrites using Mössbauer spectroscopy. In the case of ferrites having $\text{A}[\text{B}_2]\text{O}_4$ structure, their properties are mainly governed by the presence of cations which are located in two interstices between the oxygen ions. There are two types of interstices occupied by cations, called the tetrahedral (A) site and the octahedral (B) site. Origin of quadrupole splitting (ΔE_q) in ferritic spinels is considered to arise from asymmetric charge distribution at B-site. Similarly covalency effects and small distortions of oxygen tetrahedra (u -parameter) contribute to the quadrupole splitting. The state of iron in compounds having two-site spinel structure has been investigated by Mössbauer effect technique. Well established correlations between the measured isomer shift and the number of 'd' electrons in the valence band helps in determining the valence state of iron (Greenwood and Gibb 1971). We have already investigated (Jain and Darshane 1982) the crystallographic and electrical properties of the system $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ and reported its site distribution as



This paper deals with further work on the determination of the effect of distortion (u -parameter) on Mössbauer parameters and corroborates the distribution observed from x-ray and electrical conductivity data.

The end members of the system $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ were synthesized by standard ceramic techniques. High purity AR grade oxides viz Ga_2O_3 , CoO , Mn_2O_3 , ZnO and $\alpha\text{-Fe}_2\text{O}_3$ were mixed stoichiometrically and ground thoroughly in acetone. These two compounds were pelletized using polyvinylacetate as a binder and were then fired at 1173 K, sintering temperature, for a hundred hours. The samples were slowly cooled to room temperature in air (50 K/hr). The x-ray diffractometer patterns were taken on a Philips machine (pw 1051) using Cu-K_α radiation with a Ni-filter. Both these compounds (GaCoMnO_4 and ZnFeMnO_4) were then mixed in different molar proportions for the values of $X = 20, 40, 50, 60$ and 80 (where X denotes the mole percent of ZnFeMnO_4 in GaCoMnO_4) and these compositions were once again subjected to the same heat treatment. In all the cases, x-ray diffractometer patterns showed $[hkl]$ reflections due to a single spinel phase only. Our Mössbauer spectra at room temperature also showed the absence of any unreacted $\alpha\text{-Fe}_2\text{O}_3$.

The oxygen parameter (u) was calculated (Jain and Darshane 1982) from the $[111]$ reflection since it is very sensitive to u parameter value. The intensity values were calculated by varying u -parameter from 0.375 to 0.395 at intervals of 0.002 and the value matching well with the observed intensity was taken as the u parameter.

Absorbers for Mössbauer measurements were made with the samples enriched with 25% ^{57}Fe using the same procedure as above. The enriched samples also gave the same lattice parameters. Mössbauer spectra were taken with a conventional constant acceleration spectrometer operating in conjunction with a 1024-channel analyser. The calibration of the spectrometer was done with an $\alpha\text{-Fe}$ foil using 5 mCi- ^{57}Co source in a copper matrix. The enriched sample of about 20 mg was spread over a 2.5 cm diameter disc and the spectra were recorded at room temperature (294 K). The isomer shift values are expressed as mm/sec with respect to iron metal.

3. Results and discussion

For all the compositions of the system $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ (except GaCoMnO_4), well resolved quadrupole doublets were observed at room temperature indicating that all are in the paramagnetic state. The Mössbauer spectra for $X = 20, 50$ and 80 , are shown in figure 1. The isomer shift (δ) and quadrupole splitting (ΔE_q) values are summarised in table 1. All the spectra have been fitted by the least-squares method and the solid line indicates the spectrum as given in figure 1. It is observed (table 1) that the system is cubic in the range $0 \leq x \leq 60$ and tetragonal in the range $80 \leq x \leq 100$. The oxygen parameter (u) value increases with the increasing value of X in the lattice.

The isomer shift and quadrupole splitting values for ZnMnFeO_4 are found as 0.48 ± 0.02 and 0.62 ± 0.02 mm/sec relative to metallic iron respectively. Our values of isomer shift and quadrupole splitting are slightly higher than those reported earlier (Yagnik and Mathur 1968). The value of the isomer shift observed is typical of high spin ferric compounds and hence the true charge distribution of this spinel can be written as $\text{Zn}^{2+}[\text{Fe}^{3+}\text{Mn}^{3+}]\text{O}_4^{2-}$. The corresponding values of isomer shift for other compositions of the system $\text{GaCoMnO}_4\text{-ZnFeMnO}_4$ are also within the characteristic range (0.20 to 0.50 mm/sec) of high spin Fe^{3+} compounds as reported by a number of workers (Rabenau 1970; Van Loef 1966; Spencer and Scherrer 1974). Our values of

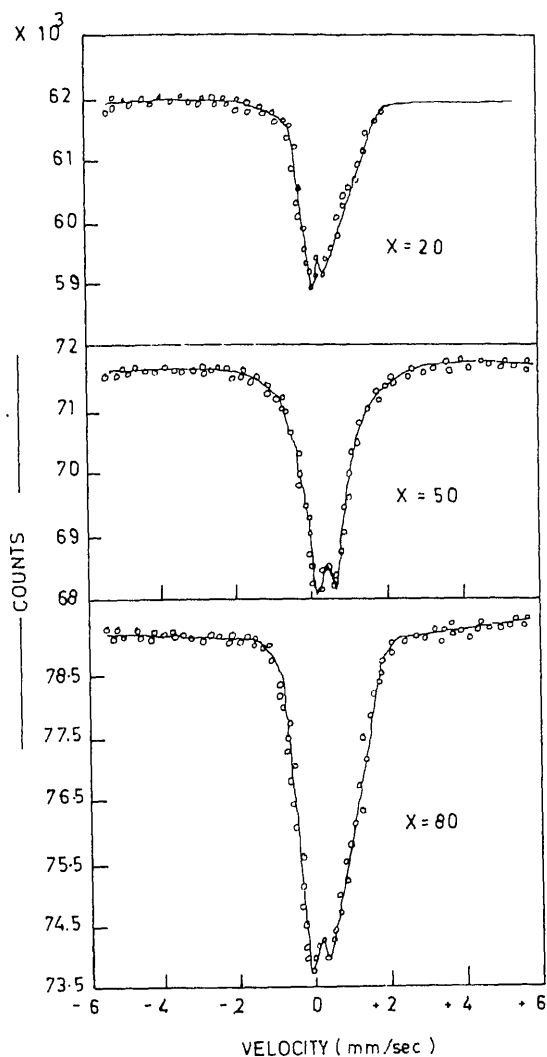


Figure 1. Mössbauer spectra at room temperature.

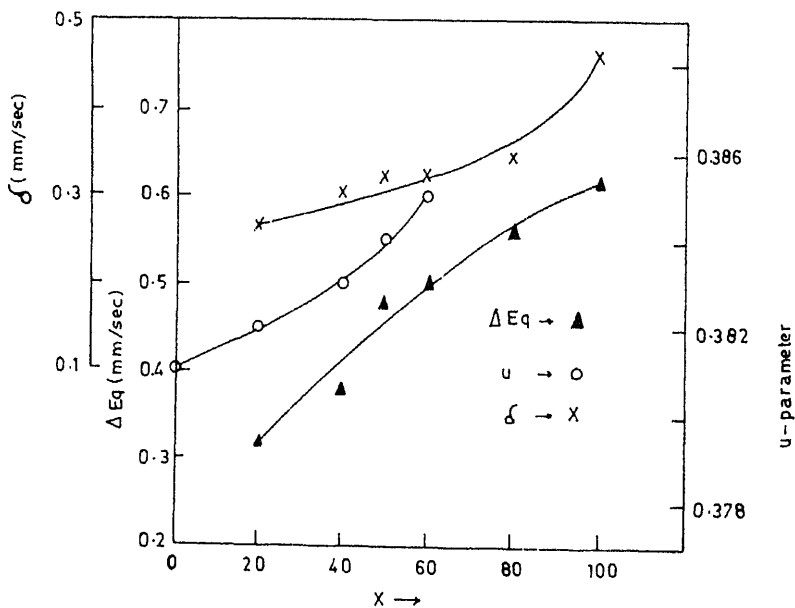
mer shift varied between 0.26 and 0.48 mm/sec with respect to metallic iron. From x-ray diffraction intensity and electrical conductivity data (Jain and Darshane 1982) it was observed that Fe^{3+} ions are predominantly present at B-site only. In the present studies no line due to Fe^{3+} is observed at the tetrahedral site. However, even if very small concentrations of Fe^{3+} are present at A-site, it would lead to a very weak signal which is not detectable in the present study.

Table 1. Lattice constant, oxygen ion parameter (u), isomer shift (δ) and quadrupole splitting (ΔE_q) values for the system $\text{ZnFeMnO}_4\text{-GaCoMnO}_4$.

(Mole %)	a (Å) ± 0.005	c (Å) ± 0.005	u ± 0.001	δ (mm/sec) ± 0.02	ΔE_q (mm/sec) ± 0.02
0	8.37	8.37	0.381	—	—
20	8.36	8.36	0.382	0.26	0.32
40	8.36	8.36	0.383	0.30	0.38
50	8.38	8.38	0.384	0.32	0.48
60	8.37	8.37	0.385	0.32	0.50
80	8.27	8.65	—	0.34	0.56
100	8.28	8.78	—	0.48	0.62

The Fe^{3+} ($3d^5$) ion will not contribute to the electric field gradient (EFG) because it is spherically symmetric. Hence quadrupole splitting should have been zero in all the compounds of the system studied. But it is gratifying to note that we have obtained sizeable quadrupole splitting in all the compounds. This is attributed to the presence of local distortion in the lattice (Mn^{3+} , $J-T$ ion). Similarly (Smit *et al* 1962) have also explained that the presence of a trigonal field at the octahedral site distorts the octahedron formed by six oxygen ions and changes the perfect cubic symmetry. This trigonal field would cause an EFG at the Fe^{3+} nucleus leading to quadrupole splitting.

The plot of quadrupole splitting (ΔE_q), isomer shift (δ), and u parameter vs composition is given in figure 2. It is seen that ΔE_q value increases with increasing u parameter. It is observed from table 1 that u parameter increases with an increase in the concentration of Zn^{2+} ion at A-site. This may be due to the replacement of Ga^{3+} by

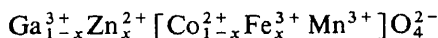


Mn^{2+} which is 20% larger in ionic radius (Shannon and Previt 1970). In this case Ga^{3+} has a tetrahedral site preference energy (Miller 1959) which is next to the Zn^{2+} ion compared to other ions in the lattice. In order to accommodate the Zn^{2+} ion in place of the Ga^{3+} ion at the A-site, tetrahedra consisting of oxygen ions expand by moving oxygen ions in the $[111]$ direction away from their nearest A-site ideal position but maintaining the cubic point symmetry. This would result in a higher value of the u parameter in the lattice. At the same time, the six nearest oxygen ions around the B-site would deviate from the cubic symmetry. This would, therefore, account for the higher order of quadrupole splitting observed with increase in X (composition). A similar trend has also been reported by Jain *et al* (1981) in the case of the system $\text{MnFe}_{1-x}\text{Mn}_x\text{CrO}_4$.

The other possible combinations like Co^{3+} , Fe^{2+} or Fe^{3+} , Mn^{4+} at the B-site can be ruled out from our isomer shift values.

Conclusions

Thus from the above discussion on Mössbauer effect studies, supported by site preference energy, x-ray intensity and electrical conductivity data as reported earlier, the site distribution of the system is given as



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Thermal decomposition of 2,4,6-trinitro anilino acetic acid and its esters

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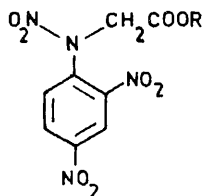
Abstract. The mode of decomposition of 2,4,6-trinitro anilino acetic acid [Glycine, N-(2,4-dinitrophenyl), N-nitro] and its methyl and ethyl esters has been determined from a study of the kinetic parameters of their thermal decomposition using DTA, isolation and identification of some of the nonvolatile products of decomposition, and confirmed from a mass spectral study. It is concluded that these compounds decompose through the scission of N-NO₂ bond.

Keywords. Explosives; nitramines; nitro anilino acetic acids; thermal decomposition.

Introduction

A number of polynitro aromatic nitramines which are potential high explosives have been reported in the literature (Fedoroff 1960). A majority of them for example pentryl, tetryl etc., have low thermal stability due to the presence of nitrate ester groups in them. Thermal decomposition characteristics of only the tetryl, of the various stable aromatic nitramines have been studied. No thermal data of any of the related aromatic nitramines are available.

Tetryl and the other aromatic nitramines reported have an alkyl group on the amino nitrogen. Hence, the explosive properties of these compounds cannot be varied extensively by bringing about small changes in the nature of the alkyl group. A compound of the structure I can be expected to offer the following advantages over tetryl and other related compounds.



- I (R = H)
II (R = CH₃)
III (R = CH₂CH₃)

being an aromatic nitramine with three nitro groups its explosive and thermal characteristics will be similar to those of the tetryl. But the explosive power is expected to be less.

Its derivatives can find use in different explosive formulations; Metal salts can be

used in delay compositions and as burning rate modifiers in propellants. Esters are useful as energetic plasticisers.

A survey of the literature revealed that only the 2,4 dinitro and the 2,4,6 trinitro derivatives of N-phenyl glycine have been synthesised so far and the N-nitro compound is as yet unreported.

In this laboratory 2,4,N-trinitro anilino acetic acid [Glycine, N-(2,4 dinitro phenyl), N-nitro (I); 2,4,N-TNAAA] and its methyl (II) and ethyl (III) esters were synthesised for the first time. Incorporation of III as the plasticiser in a cast double base propellant composition gave a propellant with improved density, burning rate and specific impulse (Rao 1982). To understand the role of this compound during the combustion of the propellant, the thermal decomposition characteristics of the acid and the two esters were studied. The results are presented in this report.

2. Experimental

2.1 Materials

2,4,N-TNAAA was synthesised by the selective N-nitration of glycine, N-(2,4 dinitro phenyl) (1084-76-0) in the presence of acetic anhydride at -7 to -5°C . Methyl and ethyl esters were obtained by the esterification of I by standard methods (Rao 1982). 2,4,N-TNAAA m. p. 161°C (decomposition) C 34.83; H 1.96; N 19.36; $\text{C}_8\text{H}_6\text{N}_4\text{O}_8$ requires C 33.56; H 2.097; N 19.58. IR (KBr) 3100, 1737, 1600, 1555, 1550, 1530, 1525, 1425, 1390, 1340, 1325, 1305 cm^{-1} . NMR Acetone d_6 δ 5 (2H); 8.1 to 8.2 (1H); 8.54 (1H); 8.7 to 8.8 (1H) and 9 (1H). Methyl ester of 2,4,N-TNAAA m. p. $126-127^{\circ}\text{C}$ C 36.8; H 2.6; N 18.4; $\text{C}_9\text{H}_8\text{N}_4\text{O}_8$ requires C 36; H 2.67; N 18.67. IR (KBr) 3125, 3000, 1745, 1610, 1565, 1560, 1550, 1535, 1422, 1355, 1320, 1300, 1240 cm^{-1} . NMR (CDCl_3) δ 3.83 (3H); 8.0 to 8.15 (1H); 8.5 to 8.6 (1H) and 8.95 (1H); signal corresponding to methylene protons not observed. Ethylester of 2,4,N-TNAAA m. p. $99-100^{\circ}\text{C}$ C 38.92; H 3.12; N 17.52; $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_8$ requires C 38.22; H 3.18; N 17.83. IR (KBr) 3122, 3000, 1755, 1615, 1562, 1555, 1545, 1535, 1422, 1357, 1345, 1315, 1295, 1240 cm^{-1} . NMR (CDCl_3) δ 1.25 to 1.45 (3H); 4.15 to 4.45 (2H); 4.8 to 5.2 (2H); 7.9 to 8.1 (1H); 8.5 to 8.6 (1H) and 8.9 (1H).

2.2 Apparatus and methods

The apparatus and experimental methods used have been described earlier (Rao *et al* 1985). Activation energies (E_a) of decomposition of the three compounds were calculated by the methods of Kissinger (1957) and Ozawa (1965). Pre-exponential factor (A), entropy of activation (ΔS^*) and the rate of decomposition (k) were also calculated. The mass spectrum of III was recorded using a Hitachi mass spectrometer; temperature of ion source- 100°C and ion current-70 eV. The major components of the nonvolatile residue obtained by the controlled decomposition of about 10 g of III were separated by column and thin layer chromatographic techniques. The components were identified by TLC and their identity confirmed by derivative preparation and IR spectroscopy (Rao 1982).

Table 1. Physical constants and kinetic parameters of thermal decomposition of 2,4,N-TNAAA and its esters.

Compound	m.p. (K) $\beta = 10 \text{ K/min}$	T_m (K) at $\beta = 5.17 \text{ K/min}$	E_a (kJ/mole)		$\ln A$	ΔS^* ($\text{J mole}^{-1} \text{ K}^{-1}$)	k (sec^{-1})
			Kissinger's method	Ozawa's method			
434 (d)		424	207.9	204.2	54.74	199	0.03511
399-400		425	182.2	179.7	46.62	131.5	0.01204
372-373		426	191.8	192.8	49.76	157.5	0.01248

peak temperature of decomposition; β = heating rate; d = decomposition

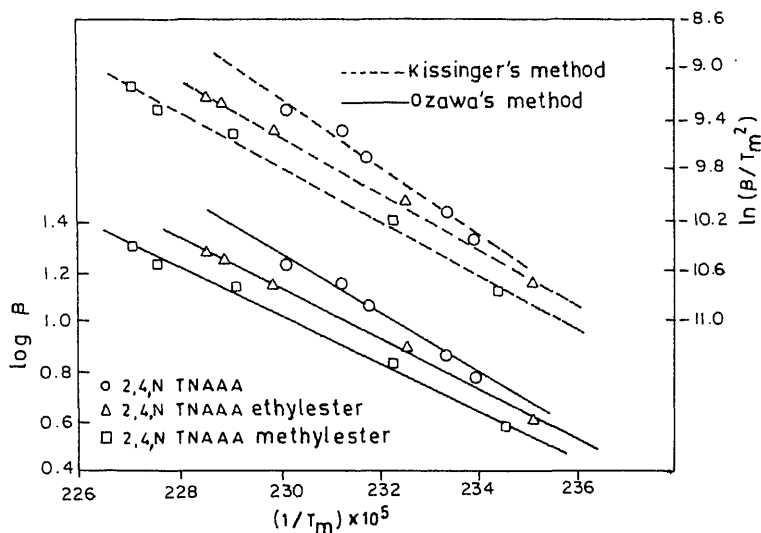


Figure 1. Arrhenius plots for the determination of kinetic parameters 2,4,N-TNAAA derivatives.

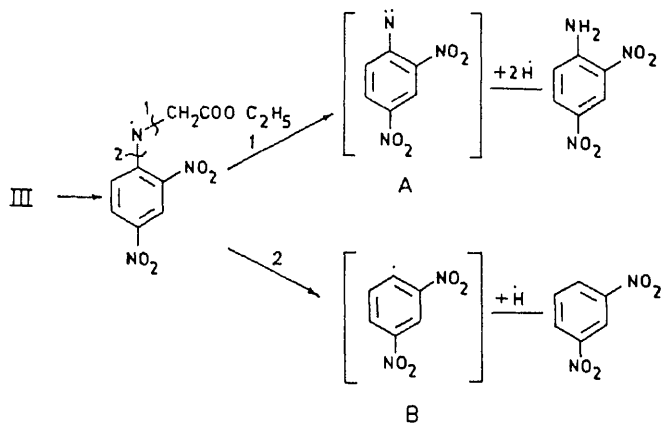
nergies are shown in figure 1. All the compounds decompose at the same temperature have kinetic parameters of the same order suggesting that irrespective of the nature R, they undergo decomposition by the same mechanism. The acid decomposes three times as fast as either of the esters. The ethyl ester of 2,4-dinitro anilino acetic acid, 2,4-dinitro aniline and *m*-dinitrobenzene are among the nonvolatile products of the decomposition of III. The formation of these products suggests that one of the three bonds $\text{N}-\text{NO}_2$, $\text{N}-\text{C}_{\text{methylene}}$ or $\text{N}-\text{C}_{\text{aromatic}}$ should rupture in the primary step of the decomposition.

The activation energy for the decomposition of the compounds I, II and III is much lower than the bond energy of the $\text{N}-\text{C}$ bond 295 kJ mole^{-1} (Roberts and Caesario 1955) and is of the same order that can be expected for the strength of the $\text{N}-\text{NO}_2$ bond. Swelley and Whitmore (1948) determined the $\text{N}-\text{NO}_2$ bond energy in ethylene nitramine to be $223.4 \text{ kJ mole}^{-1}$. It has partial double bond character due to 1.3

exhibit such tautomerism and the N-NO₂ bond in them should have a much lower strength. Further, Delpeuch and Cherville (1948) observed that when aromatic nitramines are irradiated, the excitation energy is preferentially transferred to N-NO₂ bond. Free rotation around the N-NO₂ bond in these compounds is restricted in the ground state. The preferential absorption of energy during excitation increases the bond length. This facilitates free rotation around the bond and accounts for the high energy of activation and pre-exponential factor values observed during the decomposition. These findings suggest that the cleavage preferentially takes place at the N-NO₂ bond. The NO₂ formed catalyses further decomposition accounting for the high rates of decomposition of these compounds. The preferential cleavage of the N-NO₂ bond in the nitramine decompositions is corroborated by the results of a number of workers, Flournoy (1962), Korsunski and Dubovitskii (1964), Korsunski *et al* (1967a, b, 1974) who investigated the decomposition mechanism of aliphatic nitramines with different substituents on the amino N. Several investigators using different thermoanalytical techniques studied the decompositions of nitramino explosives HMX (Robertson 1949; Rogers and Smith 1967; Maycock and Pai Vernekar 1969; Kimura and Kubota 1980), RDX (Robertson 1949; Hall 1971; Cosgrove and Owen 1974; Batten and Murdie 1970) and Tetryl (Robertson 1948; Dubovitskii *et al* 1960; Dubovitskii *et al* 1961; Merzhanov *et al* 1967). They observed that these compounds also decompose by a similar mechanism.

During the decomposition studies of tetryl, Dubovitskii *et al* (1960) isolated N-methyl 2,4,6 trinitro aniline, picric acid and 2,4,6-trinitro anisole from its decomposition products. Analogous products that can be expected from III are the ethyl ester of 2,4-dinitro anilino acetic acid, 2,4 dinitro phenol and 2,4 dinitro anisole. We have isolated the first of these compounds. A careful TLC analysis of the decomposition products of III failed to show the presence of 2,4-dinitro phenol. The formation of the other two compounds isolated in the present study can be explained as follows by the cleavage of the respective bonds and consequent reorientations arising from the high exothermicity of the primary reactions.

Thus,



the electron impact (Volk and Schubert 1968) and chemical ionisation (Zitrin and Owen 1976) mass spectra of nitramines show intense peaks corresponding to m/z 269 (NO_2) while the aromatic nitro compounds have negligible or no peaks at that value. The electron impact mass spectrum of III has an intense peak (16.7% of base peak) at m/z 269 ($M-45$) corresponding to the parent amine *viz.* ethyl ester of 2,4-DNAAA compared to a weak peak (5%) at m/z 268 ($M-46$). The formation of the parent amine in the ion source of the mass spectrometer has been observed earlier (Wilson *et al* 1970 and Larsen *et al* 1975). Larsen *et al* observed that the intensity of parent amine impurity thus increases with the temperature of the ion source and the length of the time lag from the introduction of the sample to the actual recording of the spectrum. The lower intensity of the peak at m/z 268 in comparison with that at m/z 269 can be attributed to this phenomenon. A rerecording of the mass spectrum of III using the graph method in which the time lapse is minimum gave peaks with the following intensities: m/z 269 (7.2%) and m/z 268 (30%). It can thus be concluded that the primary step in the decomposition of 2,4,N-TNAAA and its esters is the scission of the nitramine bond.

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Thermal decomposition of some nitroanilinoacetic acids

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Abstract. Thermal decomposition characteristics of 2,4 dinitroanilino acetic acid, 2,4,6 trinitro anilino acetic acid and their methyl and ethyl esters have been investigated by DTA. It is concluded from a study of the kinetic parameters of their decomposition, intramolecular hydrogen bonds existing in these compounds and mass spectral fragmentation characteristics of ethyl esters that these compounds decompose by the loss of OH through a cyclic intermediate formed by the intramolecular hydrogen bonding between the amino hydrogen atom and ortho nitro group.

Keywords. Explosives; nitroanilino acetic acids; thermal decomposition.

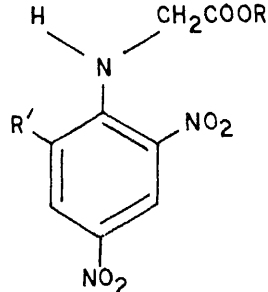
Introduction

o anilino acetic acids are the nitro derivatives of N-phenyl glycine. They are among least studied explosive compounds. No data are available on the explosive or mal properties of these compounds except for the report that their metallic salts are e explosive than the parent acids (Fedoroff 1960). The mode of thermal position of 2,4 dinitro and 2,4,6-trinitro anilino acetic acids and their methyl and esters is discussed in this report in terms of their decomposition kinetic mters and the nature of decomposition products formed, and confirmed from a y of mass spectral fragmentation of the ethyl esters.

Experimental

Samples

Dinitro anilino acetic acid [glycine, N-(2,4 dinitrophenyl), (I); 2,4-DNAAA] was ared by a minor modification of the procedure reported by Abderhalden *et al* 0). 2,4,6 Trinitro anilino acetic acid [glycine, N-(2,4,6 trinitrophenyl) (II); 2,4,6- A] was obtained by an intramolecular rearrangement of N-(2,4-dinitro-phenyl), troglycine, synthesised in this laboratory (Rao 1982). Methyl (IA, IIA) and ethyl IIB) esters of the two acids were prepared by standard methods from the respective s.



	R	R ₁	Compound
I	H	H	2,4-DNAA
IA	CH ₃	H	Methyl ester
IB	CH ₂ CH ₃	H	Ethyl ester
II	H	NO ₂	2,4,6-TNAA
IIA	CH ₃	NO ₂	Methyl ester
IIB	CH ₂ CH ₃	NO ₂	Ethyl ester

2.2 Apparatus and methods

A micro DTA apparatus specially designed and fabricated in this laboratory for experimental materials was used for the thermal analysis. The temperature measurements were made using Pt/Pt-Rh (13%) thermocouples and the heating rate (β) of the DTA furnace was monitored by a linear temperature variable rate programmer of M/s Strathclyde, Redcroft, U.K. A multispan two-pen strip chart recorder was used for recording the results. Other details of the apparatus have been described elsewhere (Rao 1982). Six samples were used for the kinetic studies. Peak temperature of decomposition (T_m) for each of the compounds at different heating rates were determined and activation energies (E_a) of decomposition calculated by the methods of Kissinger (1956) and Ozawa (1965). Mass spectra of ethyl esters were recorded using a Hitachi RMU-60 spectrometer. Temperature of the ion source: 150°C for IB and 100°C for IIA and IIB. Current 70 eV.

3. Results and discussion

Kinetic parameters of the thermal decomposition of the six compounds are tabulated in table 1. Arrhenius plots used for the calculation of activation energies are shown in figures 1 and 2.

A comparison of the thermal data of the six compounds suggests that the enthalpy of activation and entropy of activation (ΔS^*) of each of the dinitro compounds are

Table 1. Physical constants and kinetic parameters of thermal decomposition of roanilino acetic acids and their esters.

Compound	m.p. (K) $\beta = 10 \text{ K/min}$	T_m (K) at $\beta = 5.17 \text{ K/min}$	E_a (kJ/mole)		$\ln A$	ΔS^* (J mole ⁻¹ K ⁻¹)	ΔH^* (kJ mole ⁻¹)
			Kissinger's method	Ozawa's method			
I	478	469	130.1	131.6	28.45	-20.4	0
IA	399	499	156.8	159.2	33.05	17.3	0
IB	415	523	150.6	152.7	29.70	-10.9	0
II	436	462	103.4	105.6	21.92	-74.6	0
IIA	401	498	126.4	127.2	25.38	-46.4	0
IIB	364	492	111.5	116.1	21.89	-75.4	0

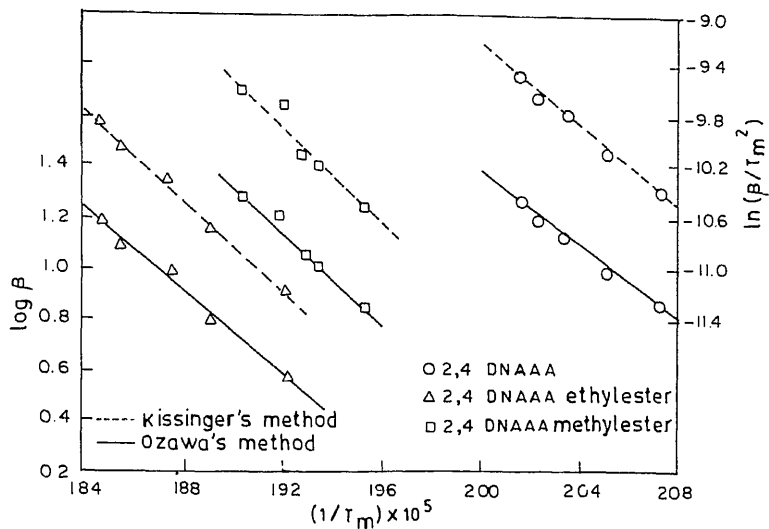


Figure 1. Arrhenius plots for determination of kinetic parameters – 2,4, DNAAA derivatives.

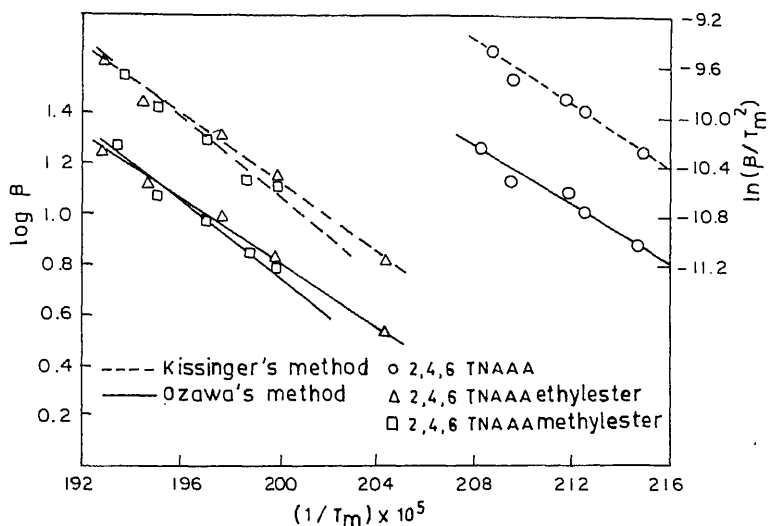


Figure 2. Arrhenius plots for determination of kinetic parameters – 2,4,6 TNAAA derivatives.

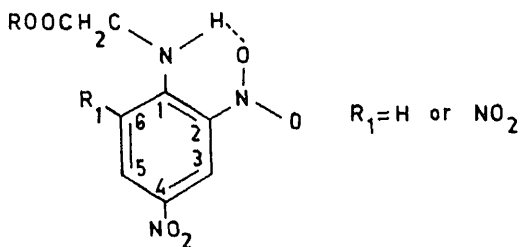
than those of the corresponding trinitro compounds thus forming two distinct groups. Except for the fact that the two acids I and II have relatively low activation energy, the nature of R appears to have little influence on the mode of decomposition. The second set of compounds differ from the first in having an additional nitro group in the 6 position which appears to facilitate decomposition as shown by the lower activation

ortho position helps in the facile formation of this intermediate and thus improves reactivity.

Decomposition reactions involving cyclic intermediates have been reported to have low entropies of activation (Kwart and Taagepara 1964; Maksimov 1969) which are of the same order as that observed for these compounds. The formation of a cyclic intermediate can thus be expected during these decompositions as well. The entropies of activation of the trinitro compounds suggest that the formation of a cyclic intermediate is further favoured by the introduction of the additional nitro group.

Another property involving the formation of a cyclic system whose strength increases by the introduction of a nitro group in the 6 position is intramolecular hydrogen bonding involving the amino H and the oxygen atom of the *o*-nitro group. A study of the influence of the solvent on the N-H stretching frequencies of IB and IIB by the method of Bellamy (1958) indicated that the introduction of the second nitro group strengthened this internal bond and resulted in shifting the N-H stretch to higher frequencies by 9 cm^{-1} (Rao 1982).

As the amino H participates in the decomposition reaction and intramolecular hydrogen bonding and the two properties namely, the entropy of activation and intramolecular hydrogen bonding are influenced by the introduction of an additional nitro group in a similar manner, it is reasonable to assume that the cyclic system formed as a result of the intramolecular hydrogen bonding is the cyclic intermediate formed in the activated state.



The primary step of decomposition then constitutes the cleavage of one or more of the endocyclic or exocyclic bonds of this cyclic system with the formation of relatively stable products. The different bonds that can be expected to undergo cleavage are $\text{C}_1\text{-C}_2$; $\text{C}_2\text{-C}_3$; $\text{C}_1\text{-C}_6$; $\text{C}_1\text{-N}_{\text{amino}}$; $\text{C}_2\text{-N}_{\text{nitro}}$; $\text{N}_{\text{amino}}\text{-H}$; $\text{N}_{\text{nitro}}\text{-O}$.

A comparison of the activation energy values of the two sets of compounds suggests that the formation of a stronger intramolecular hydrogen bond favours the decomposition. This requires the cleavage of two relatively strong bonds namely N-H and N-O , the average bond energies of these two bonds being $350.4\text{ kJ mole}^{-1}$ and $238.6\text{ kJ mole}^{-1}$ respectively (Roberts *et al* 1965). The depletion of electrons available in the ring as a result of the introduction of an additional nitro group reduces the strength of these two bonds by (i) increasing the bond length of N-H and thus weakening it and (ii) decreasing the bond order of the N-O bond of the NO_2 group, thus reducing its strength. Considering the fact that the O-H bond energy is 460 kJ mole^{-1} , the lowest activation energy observed in these compounds (104 kJ mole^{-1} for II) can only be sufficient to bring about decomposition by

From the above observations it is postulated that the primary step in the decomposition of these compounds involves the loss of the OH through a cyclic intermediate formed as a result of intramolecular hydrogen bonding between the amino H and the O atom of the *o*-nitro group. The higher activation energy of compounds I, IA and IB is due to the relatively strong N-H and N-O bonds present in them. The relatively high values of entropy of activation observed is ascribed to the greater degree of freedom available in the intermediates from these compounds due to their weaker internal hydrogen bonds.

A survey of literature indicated the absence of any reports on the mechanism of decomposition of *o*-nitroaniline derivatives. Zeman (1980) determined the kinetic parameters of the decomposition of picramide and its N-alkyl derivatives. Fields and Meyerson (1968), Maksimov (1971), Matveev *et al* (1976, 1978a) investigated the decomposition mechanism of mono- and poly-nitrotoluenes which are structurally related to the nitroanilines, Matveev *et al* (1976, 1978a) showed that the *m*- and *p*-nitrotoluenes decompose by a radical mechanism involving the cleavage of the C-NO₂ bond while the *o*-derivatives decompose through a six-membered cyclic intermediate. In a comparison of the kinetic parameters of decomposition and the study of the isotope effects of *o*-nitrotoluene and *o*-nitroaniline, Matveev *et al* (1978b) concluded that a similar mechanism operates in the case of *o*-amino nitrobenzenes as well.

Fields and Meyerson (1975) observed that the decomposition of nitro compounds under thermal conditions was similar to that under electron impact. Torssell and Hage (1965) and Musso (1967) have suggested that the decomposition reactions of explosives under electron impact closely parallel those in the early stages of explosions and that the mass spectra can therefore furnish helpful guidance in the study of such processes. Electron impact mass spectra of 2,4 DNAAA were reported by Studier *et al* (1970) and Hellberg *et al* (1972). Hellberg *et al* observed that the major fragmentation of 2,4 DNAAA was the loss of a carboxyl radical followed by the loss of an OH radical. Studier *et al* however did not report the presence of any ions corresponding to the loss of OH.

The electron impact mass spectral data of the compounds IB and IIB recorded during the present investigations are tabulated in table 2. The base peak in the mass spectra of these compounds is at *m/z* (*M*-COOCH₂CH₃). They have intense peaks

Table 2. Principal fragmentations of ethyl esters of 2,4 DNAAA and 2,4,6 TNAAA

Ethyl ester of 2,4 DNAAA Fragment	Relative intensity % base peak	Ethyl ester of 2,4,6 TNAAA Fragment ion <i>m/z</i>	Relative intensity % base peak	Possible mode of formation of ion from <i>M</i> ⁺ or (<i>M</i> + 1) ⁺
0	28.7	314	13.19	<i>M</i> ⁺
3	2.4	298	1.88	(<i>M</i> + 1) ⁺ - OH
3	0.6	268	9.04	(<i>M</i> + 1) ⁺ - OH - NO
7	26.03	242	22.62	(<i>M</i> + 1) ⁺ - COOCH ₂ CH ₃
5	100.0	241	100.0	<i>M</i> ⁺ - COOCH ₂ CH ₃
9	5.91	224	8.92	<i>M</i> ⁺ - COOCH ₂ CH ₃ - NO ₂
0	35.5	195	22.62	<i>M</i> ⁺ - COOCH ₂ CH ₃ - NO ₂

presence of relatively intense peaks at m/z 197 and m/z 242 in the mass spectra of IIB respectively whose intensity cannot be accounted for by relative abundance of isotopes only. The peak corresponding to m/z ($M - 16$) can also arise due to the loss of O from the molecular ion. The mass spectra show the loss of an OH from the ($M - \text{COOCH}_2\text{CH}_3$) ion as well, as has been observed by Hellberg *et al* (1972) in the case of 2,4 DNAAA.

It can thus be concluded that these nitro anilino acetic acids and their derivatives decompose by the loss of an OH through a six-membered cyclic intermediate.

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Photoconductivity of polymers doped with some charge transfer complexes

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Abstract. Photoconductivity of polystyrene doped with anthracene as a donor and 7,7,8,8-tetracyanoquinodimethane as acceptor was investigated by studying the photocurrent (I_{ph}), the dark current (I_d) and the sensitivity I_{ph}/I_d as the acceptor concentration changed. For this purpose a novel liquid cell was designed and successfully used for measurements. It was found that polystyrene films containing (1:10) donor-to-acceptor ratio has the greatest sensitivity as the applied charging voltage equals 0.25 volt.

Keywords. Photoconductivity; doped polystyrene; sensitivity; applied charging voltage.

Introduction

Photoconductivity measurements of samples having a high resistivity need special techniques. Such techniques are:

(a) Damber technique (Akamatu and Kuroda 1963; Hayashiy *et al* 1966; Gill 1972) by simply applying a voltage across an organic material sandwiched between two transparent or semi-transparent plates. When one of the electrodes is illuminated, carriers are generated on the surface and diffuse into the material to create a potential difference between sample and the illuminated electrode, and (b) Xerographic technique: (Mort and Emerald 1974; Williams *et al* 1975; Degorski and Kryszwski 1975a). There are two xerographic techniques commonly in use. The first involves corona charging of the surface of a polymer film cast on a suitable conductor substrate. The photoconductivity is measured by monitoring the decay in surface potential after exposure to a pulse of light. In the second method, the sample is covered by a thin layer of highly efficient photogenerating material. The rate of decay in the surface potential provides the required information.

The technique used in the present study is based on these techniques and involves applying a liquid cell (Frankevich and Sokolik 1967; Frankevich 1971) containing a thin film of the polymer between two water electrodes. The water acts as a transparent electrode (as in the Damber technique) and a parallel condenser is used to charge the electrodes instead of corona charging (as in the xerographic technique).

The rate of discharge throughout the films on applying an external illumination and in the dark has been recorded. The two discharge curves intercept each other at a point where the surface voltage is the same. The measured difference between the slopes gives information about the photoconductivity of the material used.

1.1 General formulation of the discharge characteristics

The surface potential (V_s) decays with exposure X due to the flow of photocurrent under inconstant voltage conditions. The photocurrent is controlled by two limiting mechanisms:

(i) At high potentials and low light intensity, the number of free carriers transported per transit time is small compared to (CV_s) , where (C) is the receptor capacitance. The current is emission-limited.

(ii) At a lower potential and high light intensity, the (CV_s) of the charge required to discharge the photo-receptor could traverse the sample in one transit and the current becomes space-charge limited. The emission-limited current $= J_e = eN_c$ where e is the charge on a carrier and N_c is the number of carriers emitted per unit time per unit area.

The decay time (t) of the emitted photocurrent is proportional to the product of the surface potential and its value can be given by subtracting the two slopes (V_s against t) (V against t) in the dark and in illumination.

1.2 Measuring procedure

In figure 1, curve 1 is related to the film discharge due to the dark current (J_s) and curve 2 is related to the film discharge due to the photocurrent (J_p).

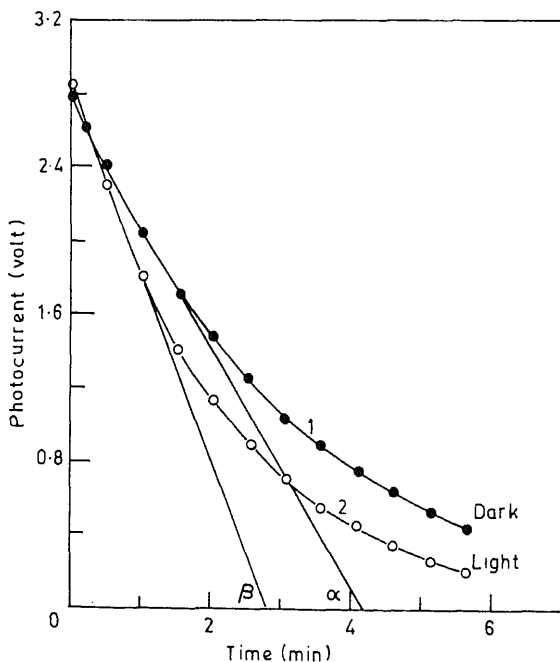


Figure 1. Photocurrent vs decay time.

2. Experimental

In the present work, the films (30μ thickness) of polystyrene doped with anthracene and TCNQ as donor and acceptor respectively, were prepared according to Degorski and Kryszewski (1975a). Figure 2 shows the schematic diagram of the apparatus used to investigate the photoconductive properties of the CT complex formed within the film. It consists of four different parts; a light source (I), a liquid cell (II), a charging circuit (III) and a measuring unit (IV). The light source (I) consists of a 200 W tungsten lamp a, for illumination of the first surface of the film, a collimating lens b, to make the illumination homogeneous, and a slit c, to minimize the stray light and acts also as a shutter. The liquid cell (II) consists of two hollow teflon parts d, f, one of them provided with a quartz window; the two parts tightly enclosing the film e. One of the two parts is filled with water as a transparent medium and acts as a first electrode. The other part is covered with a copper plate covered with graphite to make good contact with the other surface of the film. The charging circuit (III) consists of a charging unit and a capacitor (C). The measuring unit (IV) is a DC multimeter type TM9BP used for measuring the decay voltage.

3. Results and discussion

In order to investigate the capability of the system for photoconductivity measurements (anthracene, TCNQ) doped polystyrene films were used. They are known to form a CT complex in the excited state which interacts with anthracene in the ground state, producing free electrons. To study the mechanism of CT complex formed, the difference in absorption spectra of Ps + TCNQ and Ps + TCNQ + Anthracene were recorded as in figure 3. This figure shows a decrease in the absorption of anthracene as the TCNQ concentration was increased. A slight red shift in the absorption of the TCNQ of about 10 nm has been observed. This can be attributed to the formation of ionic TCNQ. TCNQ

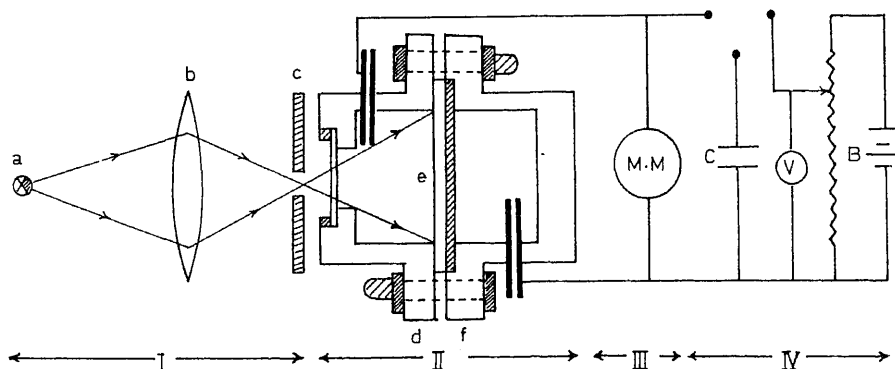


Figure 2. Schematic diagram of the apparatus used.

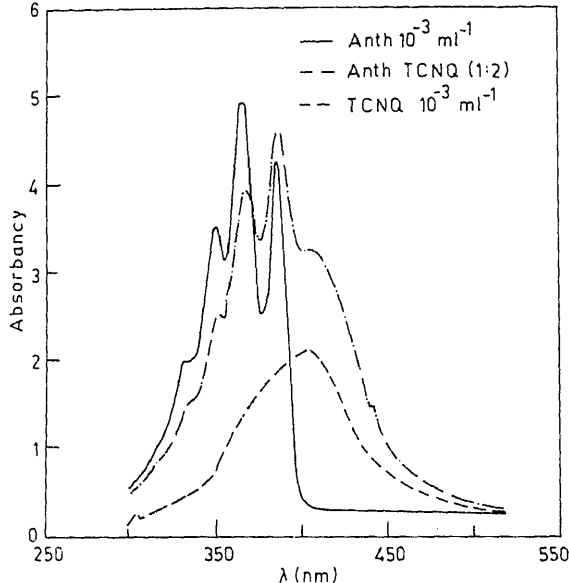
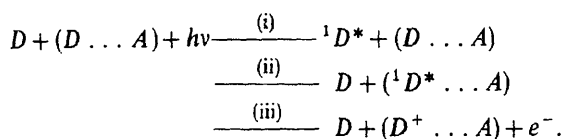


Figure 3. Absorption spectra (Anth-anthracene).

radical anion absorbs light strongly at 4200 Å, while neutral TCNQ absorbs at 3950 Å. Our results indicate the formation of a CT complex. A proposed mechanism for the formation of free electrons in similar systems was given as (Degorski and Kryszewski 1975a)



Thus it follows that the most probable mechanism of quenching is energy transfer from unbound anthracene to anthracene molecules bound in the complex. The excited acceptor centre then undergoes deactivation as a result of which charged species may arise.

In order to investigate the validity of the apparatus for measuring the photoconductive properties of the above materials which are thought to form CT complexes, TCNQ and anthracene, different acceptor concentrations were used to prepare the films, while donor concentration remains constant. The measured values of the photocurrent (I_{ph}) and the dark current (I_d) in arbitrary units as well as the ratio between them are given in table 1.

It can be seen that I_d is proportional to the applied voltage of discharge. This is in agreement with Childs law (Degorski and Kryszewski 1975b). The I_d was found to have irregular values with increasing acceptor concentration. It has maximum value as the

TABLE 1. Relative photocurrent intensity for polymer donor-acceptor systems at different conditions.

Concentration ratio mM		Charging voltage (V)	I_{ph}	I_d	I_{ph}/I_d
Anthracene	TCNQ	in volts	arbitrary units		
1	5	0.25	0.09	0.08	1.13
		1	0.08	0.021	0.38
		3	0.41	0.68	0.6
1	10	0.25	0.38	0.22	1.73
		1	0.84	0.93	0.9
		3	0.5	2.5	0.2
1	15	0.25	0.9	0.18	5
		1	1.2	0.4	3
		3	0.58	1	0.58

The observed values of I_{ph} increase as the acceptor concentration ratio is increased, while it irregularly changed with discharge voltage.

From the above conclusions it is impossible to select the most suitable photoconductive system. We therefore attempted to calculate the sensitivity of each system. At different values of V we took the known relation of sensitivity as a signal-to-noise ratio. The calculated values of (I_{ph}/I_d) (table 1) clearly indicate that the system (Ps:1 anthracene 10 TCNQ) at discharging voltage of 0.25 V is the most sensitive one.

Generally the system used was very simple and gave reliable information about the photoconductive properties of plastic films doped with π - π^* complexes. Further work is being planned to investigate other systems in the hope of finding one which can be used in a solar cell.

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Rapid Communications in Proceedings (Chemical Sciences)

From January 1985, the *Proceedings (Chemical Sciences)* publishes a new section devoted to rapid chemical communications. The objective of this section is to provide a medium for publication of novel and significant results in the different areas of chemistry which require rapid publication in order to establish priority and also to bring the work to the notice of the workers in the field without any delay. The length of such rapid communications should not exceed 4 printed pages.

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Organophosphonic acids as complexones, part III: *o*-phenylenediamine-N,N,N',N'-tetrakis- and ethylenediamine-N',N'-bis-(methylenephosphonic)acids as complexing agents

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Abstract. Polynuclear metal derivatives of *o*-phenylenediamine-N,N,N',N'-tetrakis-(methylenephosphonic)acid (PDTMP, H_8L) have been prepared in aqueous medium. The general formula of derivatives from elemental analysis is $M_4L \cdot xH_2O$ [$M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)$ and $Pb(II)$; $x = 2-8$]. Ethylenediamine-N,N'-bis(methylenephosphonic)acid (EDBMP) complexes of iron(III) $Fe_3(OH)L_2 \cdot 9H_2O$, $Fe_2(OH)_2L \cdot H_2O$ have also been studied. The electronic spectra have shown them to be six coordinated with slight distortion from octahedral geometry. Antiferromagnetism has been inferred from magnetic moment data. Infrared spectral studies have been carried out to determine coordination sites.

Keywords. Metal organopolyphosphonates; coordination sites; six coordinate.

Introduction

Ethylenepolyaminepolyphosphonic acids have been reported to have potentialities for complex formation similar to their carboxylic analogues. This is due to the donor properties of nitrogen atoms of amine and oxygen atoms, their tendency to form chelate rings and their ability to adopt various conformations according to the configurational requirements of different metal ions. In addition to this, some special structures have also been established (Kabachnik *et al* 1974) due to an increase in the number of donor atoms and the stereochemistry of the PO_3 group. However, literature includes very few studies of aminopolyphosphonic acid complexes. In view of this, in recent work, complexes of a phenylenediaminetetrakis(methylenephosphonic)acid (PDTMP) with Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Pb^{II} and of ethylenediamine-N,N'-bis(methylene-phosphonic acid (EDBMP) with Fe^{III} have been synthesised and an attempt has been made to establish their stereochemistry.

Experimental

Preparation of the ligand (PDTMP) and its sodium salt

The ligand was prepared by the method of Peck and Hudson (1969). To 2.16 g (0.02 mole) *o*-phenylenediamine, 6 ml of formaldehyde (40%) and 2.88 ml of water were added. To this mixture was then added 7.1 ml (0.08 mole) of PCl_3 dropwise with stirring, and the whole refluxed for 10 hr. The solution was then made alkaline with

sodium hydroxide and refluxed for 1 hr. On addition of acetone to this, two layers were formed. The lower layer was separated and worked up. Water was removed by evaporation and a white semisolid compound was obtained. The results of the analysis were as follows:

Found: C 17.92; H 1.71; N 4.20; and P 18.25.

Required for $\text{Na}_8\text{C}_{10}\text{H}_{12}\text{O}_{12}\text{P}_4$: C 18.19; H 1.82; N 4.25; and P 18.74%.

The free ligand was, however, prepared by replacing PCl_3 with diethylphosphite (Moedritzer and Irani 1965). The pure ligand was obtained by treating the glassy product with lead acetate and then passing H_2S gas through the lead salt solution (Westerback *et al* 1965). The result of the ligand analysis is given below:

Found: C 24.05; H 4.21; N 5.63; and P 24.85.

Required for $\text{C}_{10}\text{H}_{20}\text{O}_{12}\text{P}_4$: C 24.79; H 4.13; N 5.79 and P 25.62%.

2.2 Preparation of complexes

Bivalent metal salts (BDH AnalaR) were used as such. 0.002 moles of sodium salt of the ligand were added to an aqueous solution of 0.004 moles of a metal salt dropwise and with constant stirring. Immediate precipitation took place. The yield was improved by addition of acetone or methanol to the mixture. The precipitates were washed with 50% acetone to make the product free from metal ions and then dried at 60–70°C. The analytical data (table 1) shows the complexes as having the general formula $\text{M}_4\text{L} \cdot x\text{H}_2\text{O}$, where $x = 2-8$.

Reactions in the 1:1, 2:1 or 3:1 molar ratios of metal and ligand were also attempted without success. These always resulted in the formation of 4:1 metal-ligand complexes.

2.3 Preparation of iron(III) complexes with EDBMP

The ligand (EDBMP) was synthesized as reported earlier (Palta *et al* 1984).

(i) $\text{Fe}_3(\text{OH})_2\text{L} \cdot 9\text{H}_2\text{O}$: To 5 ml of 0.1 M ligand solution were slowly added 5 ml of 0.1 M iron(III) chloride solution and then about 5–10 ml of acetone. The solution was stirred constantly throughout. A light yellow precipitate was formed. This was washed

Table 1. Analytical and magnetic moment data of the complexes.

Complex	% Found (Reqd.)		Colour	$\mu_{\text{eff}}(\text{BM})$ at room temp.
	Metal	P		
$\text{Mn}_4(\text{PDTMP}) \cdot 2\text{H}_2\text{O}$	30.64 (30.05)	16.60 (16.94)	White	3.02
$\text{Co}_4(\text{PDTMP}) \cdot 8\text{H}_2\text{O}$	26.92 (27.55)	14.75 (14.45)	Blue-violet	2.86
$\text{Ni}_4(\text{PDTMP}) \cdot 4\text{H}_2\text{O}$	29.63 (30.01)	15.43 (15.79)	Green	1.72
$\text{Cu}_4(\text{PDTMP}) \cdot 2\text{H}_2\text{O}$	34.02 (33.17)	15.52 (16.18)	Light-blue	0.91
$\text{Zn}_4(\text{PDTMP}) \cdot 2\text{H}_2\text{O}$	33.02 (33.82)	16.92 (16.04)	White	—
$\text{Cd}_4(\text{PDTMP}) \cdot 2\text{H}_2\text{O}$	47.85 (46.77)	12.70 (12.86)	White	—
$\text{Pb}_4(\text{PDTMP}) \cdot 2\text{H}_2\text{O}$	62.85 (61.85)	9.05 (9.25)	White	—
$\text{Fe}_3(\text{OH})(\text{EDBMP})_2 \cdot 9\text{H}_2\text{O}$	19.80 (20.13)	14.50 (14.85)	Light yellow	2.54

with water till the filtrate was colourless and then dried on a water bath (50–60°C). (ii) $Fe_2(OH)_2L \cdot H_2O$: To 10 ml of 0.1 M iron(III) chloride solution 5 ml of ligand solution were added dropwise with constant stirring. 5 ml of 0.2 M Na_2CO_3 solution were then introduced. On working up, a light yellow solid was obtained.

The complexes were insoluble in water and common organic solvents and did not melt even up to 300°C. IR spectra in the form of KBr pellets were recorded on a Beckman IR-20 spectrophotometer. Mull spectra in the region 200–2000 nm were run on a DMR-21 spectrophotometer. Magnetic measurements at room temperature were made on a Gouy balance at the Panjab University, Chandigarh. Variable temperature magnetic measurements for Fe(III) EDBMP complexes were obtained from TIFR, Bombay. Thermal analyses were carried out on a Derivatograph Mom-Budapest, Hungary, type Paulik-Paulik-Erdey, OD-102. The specimens were heated at the rate of 10°/min in 20–1000° range and heated alumina was used as the standard.

The endothermic peak at about 80°C on the DTA curve shows the removal of water molecules, corresponding mass loss 2.5% (theoretical = 2.6%). On further heating up to 800°C, the organic part starts decomposing. The total mass loss of 11.25% indicates 4 $PbO \cdot P_2O_5$ (theoretical requirement 12.20%), as the composition of the residue.

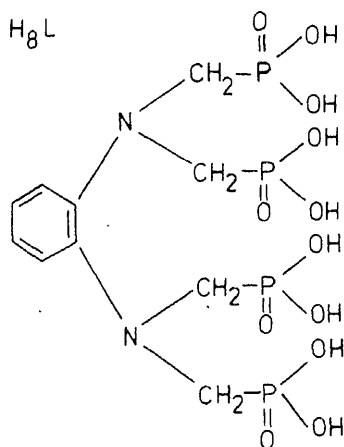


Chart 1.

3. Results and discussion

Reaction between *o*-phenylenediamine- N,N,N',N' -tetrakis(methylenephosphonic)-acid above and the different bivalent metal salts in different molar ratios in aqueous solution has always resulted in the formation of complexes containing four metal atoms attached to one ligand. The elemental analysis (table 1) has shown these complexes to have the general formula $M_4^II L \cdot xH_2O$ ($x = 2-8$; $M = Mn, Co, Ni, Cu, Zn, Cd$ and Pb). Ethylenediamine- N,N' -bis(methylenephosphonic) acid formed two complexes with iron(III) $Fe_3OHL_2 \cdot 9H_2O$ and $Fe_2(OH)_2L \cdot H_2O$. These compounds do not melt even up to 300°, nor do they dissolve in any common organic solvent. These two properties suggest that they are polymeric in nature. To establish their structure further, their infrared and electronic spectral, and magnetic measurement studies have been carried

and Wick 1977, Zhdanov and Dyanova 1965, Grayson and Grinith 1969).

The presence of two absorption bands at 1160 cm^{-1} and 1035 cm^{-1} corresponding to $\nu_{\text{as}}(\text{PO}_2)$ and $\nu_{\text{s}}(\text{PO}_2)$ respectively suggest that the free ligand exists as a zwitterion. In addition to this $\nu_{\text{as}}(\text{P-OH})$ and $\nu_{\text{s}}(\text{P-OH})$ absorptions corresponding to $-\text{P}(\text{OH})_2$ also appear at 1000 and 950 cm^{-1} . The absorption bands at 2840 cm^{-1} and 1580 cm^{-1} are assigned to the stretching and bending modes of vibration of N-H . The characteristic band of the free phosphoryl group appears at 1230 cm^{-1} .

In the IR spectra of complexes, the phosphoryl frequency gets shifted to lower values of $1105\text{--}1100\text{ cm}^{-1}$ due to the coordination of the phosphoryl oxygen to the metal ion (Khramov and Kol'tsov 1973). The stretching vibrations of the deprotonated phosphonic group $\text{PO}_3(\text{C}_2\text{v})$ give rise to two bands ν_{as} (1080 cm^{-1}) and ν_{s} (980 cm^{-1}). When M-O bonds are formed with considerable contribution from covalent forces, the ν_{as} band should undergo marked perturbation and split into two components because the symmetry of the PO_3 group is disturbed (Grigor'ev *et al* 1974). In these complexes, the two bands appear in the $1020\text{--}1070$ and $960\text{--}980\text{ cm}^{-1}$ region. The bands observed for N-H in the free ligand disappear in the spectra of metal derivatives.

3.2 Electronic spectra

The PDTMP derivative of manganese(II) is almost white and does not absorb in the $200\text{--}2000\text{ nm}$ range. The cobalt(II) complex ($\text{Co}_4\text{L} \cdot 8\text{H}_2\text{O}$) is blue-violet and its electronic spectrum gives a weak band at 7168 cm^{-1} and two at 16000 and 19420 cm^{-1} , corresponding to ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (ν_1); ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ (ν_2); ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ($\bar{\nu}_3$) transitions respectively. There is some splitting in the latter two and shoulders at 17800 and 22220 cm^{-1} are observed. This splitting is generally assumed to be due to spin-forbidden transitions. The green coloured nickel(II) complex $\text{Ni}_4\text{L} \cdot 4\text{H}_2\text{O}$ exhibits three absorption bands at 8330 cm^{-1} (${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ (ν_1), 14290 cm^{-1} (${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, ν_2), 25970 cm^{-1} (${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$, ν_3) for octahedral geometry. A band at 18520 cm^{-1} can be assigned to a spin forbidden transition ${}^1\text{E}_g \leftarrow {}^3\text{A}_{2g}$. The absorption spectrum of blue coloured $\text{Cu}_4\text{L} \cdot 2\text{H}_2\text{O}$ consists of a broad band at 13330 cm^{-1} and is attributed to the transition ${}^2\text{T}_{2g} \leftarrow {}^2\text{E}_g$. The band is asymmetric on account of splitting by a low symmetry ligand field component.

It is difficult to assign any stereochemistry to iron(III) (d^5 system) in EDBMP complexes in the absence of the oscillator strength of various bands as is the case with Mn^{II} EDBMP complexes (Palta *et al* 1984).

3.3 Magnetic moments

The magnetic moment of the Mn(II) complex is 3.02 BM (297°K). This value is much lower than the spin only value for a d^5 system (5.92 BM) and suggests the presence of antiferromagnetic exchange. The direct orbital-orbital overlap of neighbouring metal ions is also possible, because the polymeric character can bring these metal ions to distances close enough for interaction. However, the possibility of super exchange via PO_3 bridges is not ruled out. The magnetic moment of the cobalt(II) complex at room temperature (2.86 BM) as compared to the normal moments ($4.30\text{--}5.20\text{ BM}$) again

shows the presence of an appreciable antiferromagnetic exchange interaction. The normal magnetic moment value of 1.72 BM for the nickel(II) complex (spin only value of d^8 -2.83 BM) indicates that the system is magnetically concentrated. $\text{Ni}_4\text{L} \cdot 2\text{H}_2\text{O}$ has the magnetic moment value of 0.91 BM at 297°K, which is much lower than the normal value (1.70–2.20 BM) and is probably due to antiferromagnetic exchange arising from Cu–Cu interaction or via super exchange.

Magnetic moments at different temperatures for the iron complexes with ethylenediamine- N,N' -bis(methylenephosphonic acid) were determined. It was observed that there was decrease in magnetic moments with decrease in temperature as is also expected for antiferromagnetic complexes (table 2) (Ranbore *et al* 1982). From this observation antiferromagnetism may be inferred for other complexes also.

$\text{Zn}_4\text{L} \cdot 2\text{H}_2\text{O}$, $\text{Cd}_4\text{L} \cdot 2\text{H}_2\text{O}$ and $\text{Pb}_4\text{L} \cdot 2\text{H}_2\text{O}$ are diamagnetic as expected. The corresponding mercuric complex could not be prepared as the addition of the ligand to HgCl_2 solution first reduces it to Hg_2Cl_2 and then to Hg.

Thermal analyses

Thermal behaviour of these complexes is almost the same, hence, only that of $\text{Ni}_4\text{L} \cdot 2\text{H}_2\text{O}$ is being discussed here in detail. There is a broad endothermic peak at about 80°C and corresponds to a mass loss of 2.5 % due to removal of water molecules (theoretical required 2.6 %). The DTG curve shows a sharp peak at 170° paralleled by a long exothermic peak. The compound undergoes a further mass loss of 5 %, perhaps due to the decomposition of organic part. The DTG curve shows no more clear steps and mass loss is also gradual upto 800°C. However, a large number of peaks with endothermic effects are seen on DTA curve—360°, 400°, 420°, 490° and 570°C. At 640°C, there is a slight endothermic effect. The total mass loss of 11.25 % indicates the formation of $2\text{PbO} \cdot \text{P}_2\text{O}_5$ as the composition of the residue (theoretical required: 12.0 %). Such conclusions have also been drawn by Khramov and Kol'tsov (1973) in case of rare earth element complexes with 1-hydroxyethylidenediphosphonic acid.

Table 2. Magnetic moment data at different temperatures for EDBMP complexes of iron(III).

Temperature (K)	Magnetic moment μ_{eff} (B.M.) of $\text{Fe}_3(\text{OH})(\text{EDBMP})_2 \cdot 9\text{H}_2\text{O}$	Temperature (K)	Magnetic moment μ_{eff} (B.M.) of $\text{Fe}_2(\text{OH})_2(\text{EDBMP})_2 \cdot \text{H}_2\text{O}$
14.0	1.259	14.4	1.5685
14.6	1.266	15.0	1.585
20.6	1.5123	20.8	1.738
24.0	1.5416	24.2	1.7605
28.0	1.578	27.8	1.8345
31.2	1.5823	31.4	1.8795
41.4	1.58	41.0	1.9325
86.0	1.908	86.0	2.25

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polarographic study of zinc-thiocyanate complexes in mixed solvents

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Abstract. Complexes of zinc with thiocyanate were studied polarographically in aqueous mixtures of methanol, ethanol, dioxan and dimethyl formamide (DMF). The reduction, in most cases, was not reversible and the degree of irreversibility increased with the percentage composition of the mixed solvent as well as with the nature of the solvent in the order: alcohols < dioxan $\approx$ DMF. The 'formal' potentials for reduction, determined by amalgam polarography at different thiocyanate concentrations in each solvent mixture, were used to calculate the standard rate constant, k_s , and the transfer coefficient, α , for the reduction from the current-potential data. The stability constants of the complexes, also evaluated from the 'formal' potentials, varied linearly with the dielectric constant of the medium.

Keywords. Polarography; zinc-thiocyanate; mixed solvents.

1. Introduction

The scope of voltammetry has been extended, in recent years, by increasing use of non-aqueous solvents. The physical properties of the solvent such as viscosity, dielectric constant, etc., have a pronounced effect on diffusion as well as electron transfer processes. The double layer structure is altered by the solvent thus affecting the electrode reaction. Moreover, in many cases the tendency of metal ions to form complexes with ligands shows significant variations in different solvents.

The low solubilities of inorganic electrolytes in nonaqueous solvents pose special problems but these are circumvented by the use of aqueous mixtures of these solvents. Also, the use of mixed solvents enables one to study the progressive replacement of water by the solvent.

Thiocyanate complexes of metals are of importance in analytical chemistry (Sultanova *et al* 1973). They are of moderate stability and hence form excellent systems for the study of complexation characteristics in mixed solvents. A polarographic study of zinc-thiocyanate complexes in aqueous mixtures of methanol, ethanol, dioxan and dimethylformamide (DMF) is reported in this paper.

2. Experimental

A stock solution of zinc sulphate (BDH AR) was standardised with EDTA. Lithium nitrate (Allied and Co., Bombay, LR) was purified by pre-electrolysis and was estimated by an

ion-exchange procedure. Methyl alcohol (BDH AR) was used as such. Ethyl alcohol and DMF (Koch-Light, England) were freshly distilled before use. Dioxan (E Merck, pro Analysis) was dried, refluxed over sodium hydroxide and then fractionally distilled before use. Potassium thiocyanate (Sarabhai Chemicals, GR) was used without purification and the stock solution was estimated by titration with silver nitrate.

Current potential curves were obtained at $30 \pm 0.1^\circ\text{C}$ on a manual set-up with a saturated calomel electrode (SCE) as the reference electrode. The reported currents have been corrected for the residual current. Viscosity measurements were made with an Ostwald's viscometer.

3. Results and discussion

Polarograms of $4 \times 10^{-4}\text{ M}$ zinc were recorded in the absence and presence of thiocyanate in 10, 25 and 50% (v/v) aqueous mixtures of methanol, ethanol, dioxan and DMF. The ionic strength was maintained at 1.0 with lithium nitrate.

Well-defined waves were obtained in all the media except in 50% DMF. The half-wave potentials were shifted to more negative values with increasing thiocyanate concentration. The reduction, however, was reversible only in 10% methanol, ethanol and DMF and in 25% methanol. Log-plots with curvature or high slopes in other media indicated quasi-reversible or irreversible processes.

The reversibility of the reduction was further investigated by calculating the standard rate constant, k_s , and the transfer coefficient, α . The 'formal' potentials, required for this purpose, were obtained from composite polarograms of zinc, recorded in different media, using a dropping zinc amalgam electrode. The kinetic parameters, k_s and α , were then evaluated from the data on cathodic waves by means of the expressions (Randles 1959),

$$i/i_d = \frac{1}{2} \left[1 + \tanh \left(-\frac{\beta\eta}{2} \right) \right] \phi(H) \quad (1)$$

and

$$\log \left[\frac{h}{(1 + \exp \beta\eta)} \right] = \log \left[\left(\frac{3}{7D} \right)^{1/2} k_s \right] - \frac{\alpha\beta\eta}{2.303}, \quad (2)$$

where β stands for nF/RT and η for $E - E_f^0$ (E_f^0 being the 'formal' potential) $\phi(H)$ is a function of H which is read from a plot of $\phi(H)$ vs H (Milner 1957). H is given by

$$H = h \cdot \tau^{1/2}, \quad (3)$$

where τ is the drop time. Thus, the parameter H (and hence, h) obtained from the current-potential data, yielded k_s and α from a plot of $\log [h/(1 + \exp \beta\eta)]$ vs η (equation 2).

It was observed from the current-potential data for the reduction of zinc in the presence of thiocyanate in different mixed solvents that the $E_{1/2}$ and E_f^0 were almost the same, in 10% methanol, ethanol and DMF, and in 25% methanol, which indicated reversible reduction. Calculation of k_s and α in other media was done by means of (1) and (2) and the values are presented in table 1.

Table 1. Values of α and k_s in different media.

S/M	Methanol			Ethanol			DMF			Dioxan			50%		
	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α
0.38	—	2.79	—	—	0.40	3.44	0.41	2.89	0.36	3.22	0.36	2.79	—	—	—
—	—	—	0.28	2.53	0.34	3.76	—	—	—	—	0.36	2.70	0.50	3.74	—
0.34	0.38	3.01	0.38	2.88	—	—	0.33	3.01	0.45	2.99	0.40	2.90	0.55	3.90	—
—	—	—	0.30	2.70	0.37	4.00	—	—	—	—	0.34	3.01	—	—	—
0.34	—	3.41	—	—	—	—	0.36	3.21	0.50	2.97	—	—	0.63	4.19	—
—	—	—	0.38	3.10	—	—	—	—	—	—	0.40	3.23	—	—	—
0.36	—	3.56	—	—	—	—	0.41	3.37	0.49	2.94	—	—	—	—	—
—	—	—	0.40	3.08	—	—	0.37	3.40	—	—	0.40	3.28	0.52	4.21	—
0.36	—	3.65	—	—	—	—	—	—	0.51	2.98	—	—	—	—	—
—	—	—	0.44	3.16	—	—	0.33	3.43	—	—	0.42	3.33	0.57	4.34	—
—	—	—	—	—	—	—	0.43	3.37	0.48	2.87	0.42	3.34	—	—	—

Table 2. Values of stability constants and the product $I\eta^{*1/2}$ in different media.

Solvent %	$\frac{1}{\epsilon} \times 10^2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	I	$I \cdot \eta^{*1/2}$
Methanol							
10	1.33	—	1.78	—	2.57	1.24	1.36
25	1.43	—	1.93	1.98	2.70	1.10	1.35
50	1.67	—	—	2.90	4.48	1.04	1.36
Ethanol							
10	1.35	—	1.78	—	2.57	1.18	1.36
25	1.49	—	2.00	2.00	2.94	0.99	1.37
50	1.89	—	—	4.38	4.72	0.86	1.37
DMF							
10	1.31	—	1.78	—	2.57	1.20	1.33
25	1.37	—	—	—	3.90	1.01	1.25
Dioxan							
10	1.43	—	1.78	—	2.57	1.19	1.30
25	1.75	—	1.60	2.40	3.14	1.04	1.29
50	2.80	—	—	4.81	4.83	0.87	1.26

and DeFord and Hume (1951) using E_f^0 in the place of $E_{1/2}$, are tabulated in table 2.

The properties of the solvent that affect the polarographic behaviour are, mainly, the dielectric constant and viscosity, though chemical reactivity also plays a part. Ion pair formation between the depolarizer and the supporting electrolyte ions is enhanced in media of low dielectric constant. It has been observed in this study that the reversible half-wave potential, $E_{1/2}^r$ or the 'formal' potential, E_f^0 of the uncomplexed zinc is more positive than in water for all solvent mixtures. The shift in $E_{1/2}^r$ to positive values has been observed earlier (Schaap *et al* 1955; Koptenko and Migal 1975) and can be explained on the basis of electrostatic theory of solvation. The linear plot of E_f^0 vs $1/\epsilon$ where ϵ is the dielectric constant of the medium indicates a rough correlation between the electrostatic part of the free energy of transfer, ΔG_i^0 , from water to aqueous mixtures of the solvent and $(1/\epsilon)$ (Born 1920).

Since stability constants are related to E_f^0 , an attempt was made to correlate the stability constants with the dielectric constants of the media. The fourth species was identified in all the cases and hence a plot of $\log \beta_4$ vs $(1/\epsilon)$ was obtained which resulted in straight lines. Similar behaviour has been observed for a number of metal complexes (Arevalo, *et al* 1975; Tur'yan 1956, 1959, 1960).

The diffusion coefficients of the electroactive species are influenced by ion-solvent interaction which is manifest in the form of solvation and viscosity effects. The viscosity effect can be expressed by the Stokes-Einstein equation (1920) as

$$D = (RT/N)(1/6\pi\eta^*r), \quad (4)$$

where η^* is the viscosity of the medium. Since i_d is proportional to $D^{1/2}$, the constancy of the product, $i_d\eta^{*1/2}$ indicates that the charge in diffusion current is mainly due to viscosity effects. In the present work, dropping mercury electrodes with different capillary characteristics were used. Hence, the diffusion current constant, I , equal to $i_d/m^{2/3}\tau^{1/6}$, was substituted for $i_d \cdot I \cdot \eta^{*1/2}$ was constant in alcohol media while it

The decrease in k_s in the presence of thiocyanate in the different media studied indicates the increasing role of the solvent in influencing the double layer structure as well as the electron transfer processes. The adsorption of the solvent and the preferential solvation of the electrode or the cation may result in the partitioning of the cation between the bulk of the solution and the interface, thereby influencing the electrode reaction (Behr *et al* 1979). An interesting observation was that while well-developed waves were obtained in dioxan (dielectric constant ~ 35), a drawn out and ill-defined wave was observed in 50% DMF with much higher dielectric constant (~ 65). This may be due to the chemical reactivity of DMF, in which zinc is extensively solvated, which hinders the reduction.

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Synergism in the extraction of lanthanides, copper and thorium in the presence of HTTA and antipyrine

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Abstract. Synergism in the extraction of lanthanum, europium, lutetium, copper and thorium has been studied using a mixture of HTTA and 2,3-dimethyl, 1-phenyl pyrazol-5-one (antipyrine). Synergism was observed in all the cases except copper. The nature of extracted species has been determined on the basis of log-log plots and the equilibrium constants for the adducts have been evaluated. Antipyrine has been found to be a good donor comparable in strength to other alkylphosphorus donors.

Keywords. Synergism; extraction of metals; HTTA; antipyrine.

Introduction

Studies on the extraction of uranium with a mixture of a β -diketone and antipyrine (2,3-dimethyl, 1-phenyl pyrazol-5-one) indicated the potentialities of antipyrine as a synergist (Malhotra *et al* 1984). Antipyrine is of considerable importance in medicine and other substituted pyrazolones are also attracting attention as β -diketones in extraction studies. In order to investigate the usefulness of antipyrine as a synergist, the extraction of metal ions having different valence states, such as lanthanum, europium, lutetium, copper and thorium was studied from benzene media, the results of which are reported in this paper.

Experimental

Extraction experiments were carried out at 30°C at an ionic strength of 0.5 using sodium chloride. The extraction procedure has been described earlier (Malhotra *et al* 1984). The metal ions were estimated spectrophotometrically using thoron for thorium, ceric nitrate for rare earths and diethyldithiocarbamate for copper using standard methods.

Results and discussion

In order to study the extraction behaviour of trivalent lanthanides, extraction of lanthanum, europium and lutetium as representatives of light, middle and heavy rare

earths was studied. The pH was maintained at 4.2 and the distribution ratio was measured as a function of concentration of HTTA and antipyrine APY.

3.1 Rare earths-HTTA-APY system

Extraction of La, Eu and Lu with HTTA was quite low but addition of APY resulted in considerable enhancement in the extraction. The results for the extraction of La are shown in figure 1. The concentration of HTTA was varied keeping pH constant at 4.2 and $[APY]_{tot}$ at 0.008 M. The concentration of APY was also varied keeping HTTA constant at 0.02 M. The concentration of HTTA in the organic phase was calculated taking into account its partition coefficient of 54 (Sekine *et al* 1973). The concentration of $[APY]_0$ was calculated taking into account the partition coefficient of 0.525 and pK of 1.38 which were determined in a separate series of experiments. The plots of $\log D$ vs $\log [HTTA]_0$ resulted in a straight line with a slope of 2.6 while that of $\log D$ vs $\log [APY]_0$ resulted in a curve with the slope changing from zero to two. The results indicated the formation of an adduct having one to two molecules of APY. The data were analysed to evaluate the nature of the adduct.

The distribution ratio, D can be written as

$$D = \frac{[La A_3]_0 + [La A_3 APY]_0 + [La A_3 (APY)_2]_0 + \dots}{[La^{+3}]} \quad (1)$$

where A represents the anion of HTTA. Expressing (1) in terms of equilibrium constants of the adducts and on rearranging, we get

$$F_0 = \frac{D[H^+]^3}{[HA]^3} = K_{30} + K_{31}[APY]_0 + K_{32}[APY]_0^2, \quad (2)$$

where K_{3n} represents the equilibrium constant for the formation of $[La A_3 (APY)_n]_0$. Hence a plot of F_0 vs $[APY]_0$ can be used to evaluate the equilibrium constants for adduct formation. The plot resulted in a smooth curve (figure 1), which was utilised to calculate equilibrium constants summarised in table 1.

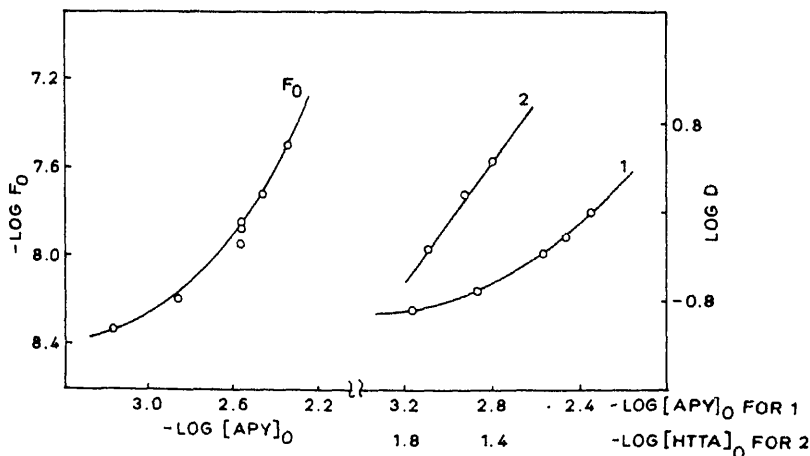


Table 1. Values of equilibrium constants.

Metal	μ	log equilibrium constant				
		K_{30}	K_{31}	K_{32}	K_1^*	K_2^*
La(III)	0.5	-8.25	-6.00	-2.92	2.52	6.56
Eu(III)	0.5	-8.30	-3.87	-0.31	4.43	7.99
Lu(III)	0.5	-7.05	-2.24	1.60	4.81	8.65
Th(IV)	1.0	1.10*	6.60†	—	5.50	—

* log K_{40} ; † log K_{41} .

Similar experiments were carried out using europium and lutetium and the results indicated the formation of two adducts. The values of equilibrium constants are summarised in table 1. Earlier studies on synergism in the extraction of europium (Sudersanan and Sundaram 1981a, b) with various donors indicated the formation of a diadduct with alkylphosphorus donors and sulphoxides while a monoadduct was indicated with nitrogen donors. The formation of both the adducts is indicated with all the three metals reported here. This is in agreement with the observation that antipyrine is intermediate in donor strength between nitrogen donors and alkylphosphates, as indicated by the extent of synergism.

The adduct formation constant K_n^* represented by



where S is a donor, was also evaluated as $K_n^* = K_{3n}/K_{30}$. The values are summarised in table 1 and increase in the order $\text{La} < \text{Eu} < \text{Lu}$, which is in agreement with the increasing ionic potential of the metal ions. The equilibrium constants as well as the adduct formation constants increase with increase in atomic number indicating a greater separation factor between individual rare earths in the case of synergistic systems compared to β -diketones alone.

3.2 Copper-HTTA-APY system

Investigations were also extended to copper as a representative of divalent metal ions. Extraction of copper with HTTA both in the presence and absence of APY indicated that the enhancement in extraction was not significant. A comparative study was also made using TOPO, TPPO and TBP and the absence of appreciable synergism in all the cases indicated that the coordination number for copper did not change to a value higher than four in presence of moderate concentrations of the donor.

3.3 Thorium-HTTA-APY system

Synergism in the presence of APY was also investigated in the case of thorium, a tetravalent element. The distribution ratio was measured as a function of pH and

and 1 respectively indicating the formation of $\text{Th}(\text{TTA})_4 \text{APY}$. The equilibrium constant was evaluated as $10^{6.6}$. The equilibrium constant for the extraction of thorium by HTTA alone was estimated at $10^{1.1}$ and hence $\log K_1^*$ was calculated as $10^{5.5}$ indicating synergism to be quite pronounced. The coordination number of thorium is likely to increase to nine as in the case of other donors like TBP, TOPO etc.

The above results indicate the suitability of antipyrine as a neutral donor in extraction studies. It has advantages over other donors, being a compound with high water solubility and being equally effective in causing synergism to the extent observed with neutral donors. In view of its low cost and easy availability it has potential applications in the extractive separation of metal ions. A separation of thorium and the rare earths is of interest since they occur together. The results indicate that they can be separated easily and the separation factor of lighter rare earths is enhanced by the use of synergistic systems.

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Role of aqueous DMSO in resolving 'proton ambiguity' in the formation of iron(III) complexes of iron(III)

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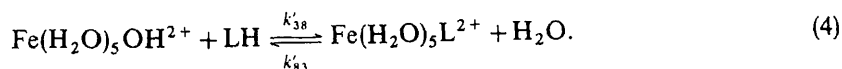
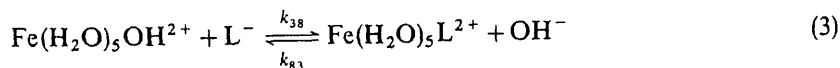
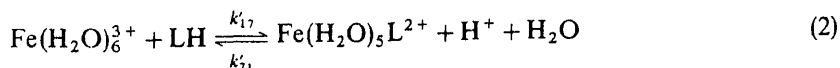
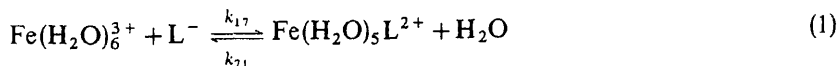
MS received 17 November 1984

Abstract. The formation of FeL^{2+} ($\text{L}^- = \text{N}_3^-, \text{SCN}^-$) in H_2O -dimethylsulphoxide (DMSO) mixtures was studied by equilibrium, stopped flow and temperature jump observations. The acid dissociation constants associated with LH and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and the formation constants associated with FeL^{2+} were determined at various solvent compositions. In kinetic studies, the solvent composition dependence of the overall equilibration rate was explained in terms of equations predicted by a reaction scheme which includes DMSO coordinated species. Analysis of results on the basis of these equations identified $\text{Fe} \cdot \text{OH}^{2+} \cdot \text{HN}_3$ and $\text{Fe}^{3+} \cdot \text{SCN}^-$ as the dominant transition states contributing to pH-independent paths of formation of FeL^{2+} in the cases of N_3^- and SCN^- respectively. Thus, the results which support the Eigen-Tamm-Wilkins mechanism have resolved the mechanistic ambiguity in the pH-independent paths of formation of FeL^{2+} . It is also shown that we cannot neglect species such as $\text{FeOH} \cdot \text{HN}_3^{3+}$, $\text{Fe} \cdot \text{OH} \cdot \text{N}_3^+$ and $\text{Fe} \cdot \text{HN}_3^{3+}$ while accounting for the kinetic behaviour.

Keywords. Proton ambiguity; iron(III) complexes; aqueous DMSO; temperature jump; stopped flow.

Introduction

When a molecule in the protonated state reacts with a second molecule in the protonated state in aqueous solutions, the pH dependence of the observed equilibrium and of the kinetic parameters does not indicate which of the two molecules is protonated before the formation of the transition state or as a constituent of the transition state (Frost and Pearson 1961; Espenson and Dustin 1969; Accasina *et al* 1967; Calvaruso *et al* 1978; Cavasino 1968). For example, the possible paths of formation of $\text{Fe}(\text{H}_2\text{O})_5\text{L}^{2+}$ from $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and the unidentate ligand L^- are as follows:



$$1/\tau B = k_{17} + (k'_{38} K_H)/K_{LH} + (k_{38} K_H)/[H^+] + (k'_{17}[H^+])/K_{LH} \quad (5)$$

for the reaction schemes shown in (1)–(4). K_H and K_{LH} are dissociation constants for the protonation equilibria $\text{Fe}(\text{H}_2\text{O})_6^{3+} \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ and $\text{L}^- \rightleftharpoons \text{LH}$ respectively. B depends on the equilibrium concentrations of the reactants and the formation constant $K_S (= k_{17}/k_{71})$ (the expression for B is given in §3). Paths (1) and (4) contribute to the pH independent part of $1/\tau B$. Thus a study of the pH dependence of $1/\tau B$ in aqueous solutions cannot tell us the relative magnitudes of these two contributions. There have been some attempts to remove such proton ambiguities (Accasina *et al* 1967; Calvaruso *et al* 1978). In this paper, we show that a preferred answer to this problem could be obtained for the kinetics of formation of $\text{Fe}(\text{H}_2\text{O})_5\text{L}^{2+}$ ($\text{L}^- = \text{N}_3^-$, SCN^-) by a study in H_2O -DMSO mixtures (DMSO = dimethylsulphoxide). This has been possible due to the ability of H_2O -DMSO mixtures to alter K_H/K_{LH} without significantly affecting the rate constants (Krishnamoorthy and Prabhananda 1981). The presence of DMSO undoubtedly increases the complexity of the system. However, our analysis of the kinetic data shows that this complexity can be accounted for by additional terms in the expression for the kinetic parameters.

2. Experimental

The spectrophotometric titrations were carried out using a Cary 17D spectrophotometer. T -jump relaxations were studied using a home-made instrument (Prabhananda 1977). The kinetic spectrophotometer of the T -jump instrument was also used for monitoring the concentration changes in stopped flow experiments. The driving syringes, ratio drive mechanism, mixing chamber and observation chamber assembly of the stopped flow set up had been obtained from Hi-Tech (England). A pneumatic drive made in our laboratory was used for driving the syringes. The metal ion concentration was sufficiently small such that the change in the transmitted light due to complex formation could be directly related to concentration changes in stopped flow experiments. The stopped flow experiments were carried out at sufficiently high ligand concentration (or buffered) such that it could be treated as a constant. The stopped flow traces obtained under such conditions were single exponentials with time constants τ . These were determined by the procedure described elsewhere (Prabhananda 1978). Chemicals used and the preparation of reaction mixtures are described in our earlier papers (Krishnamoorthy and Prabhananda 1981; Prabhananda 1978). The ionic strength was regulated at $\mu = 1.0$ using NaClO_4 . Observations were made at 25°C and $\text{pH} = -\log [H^+]$ was used in the evaluation of pH dependent quantities. The K_{LH} associated with N_3^- were determined for convenient solvent mixtures by monitoring the pH as a function of the volume of a strong acid (HCl) added in preparing the solutions. In the case of the ligand SCN^- , the extent of change in K_{LH} with solvent composition was estimated by monitoring the change in absorbance of thiocyanate solutions at 250 nm (Morgan *et al* 1965). The metal ligand complex formation constants were estimated by using optical density (OD) vs $\text{OD}/[\text{L}^-]$ plots (Krishnamoorthy and Prabhananda 1981).

3. Results and discussion

The general reaction scheme for the formation of $\text{Fe}(\text{H}_2\text{O})_5\text{L}^{2+}$ in H_2O -DMSO mixtures is shown in figure 1. Coordination of water molecules is not depicted in order to reduce the complexity. Reactions (1)–(4) correspond to the boxed region of figure 1. Various equilibrium constants used in this work are defined in the figure. Analysis of kinetic data to elucidate the dominant pH-independent path (5) requires the knowledge of equilibrium constants K_{H} , K_{LH} and K_{S} .

3.1 Acid dissociation constants K_{H} and K_{LH} :

The acid dissociation constants K_{H} associated with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ in various H_2O -DMSO mixtures were determined in our previous work (table 1 in Krishnamoorthy and Prabhananda 1981). These can be related to the mole fraction of DMSO, f , by a linear equation

$$pK_{\text{H}} = (1-f)pK_{\text{H}}^{\text{O}} + fpK_{\text{H}}^{\text{I}} \quad (6)$$

with $pK_{\text{H}}^{\text{O}} = 2.53$ and $pK_{\text{H}}^{\text{I}} = 19.9$. Similarly the acid dissociation constants K_{LH} associated with the ligands in H_2O -DMSO mixtures fit the equation

$$pK_{\text{LH}} = (1-f)pK_{\text{LH}}^{\text{O}} + fpK_{\text{LH}}^{\text{I}} \quad (7)$$

with $pK_{\text{LH}}^{\text{O}} = 4.15$ and $pK_{\text{LH}}^{\text{I}} = 7.5$ for N_3^- and $pK_{\text{LH}}^{\text{O}} = -1.85$ and $pK_{\text{LH}}^{\text{I}} = 3.5$ for

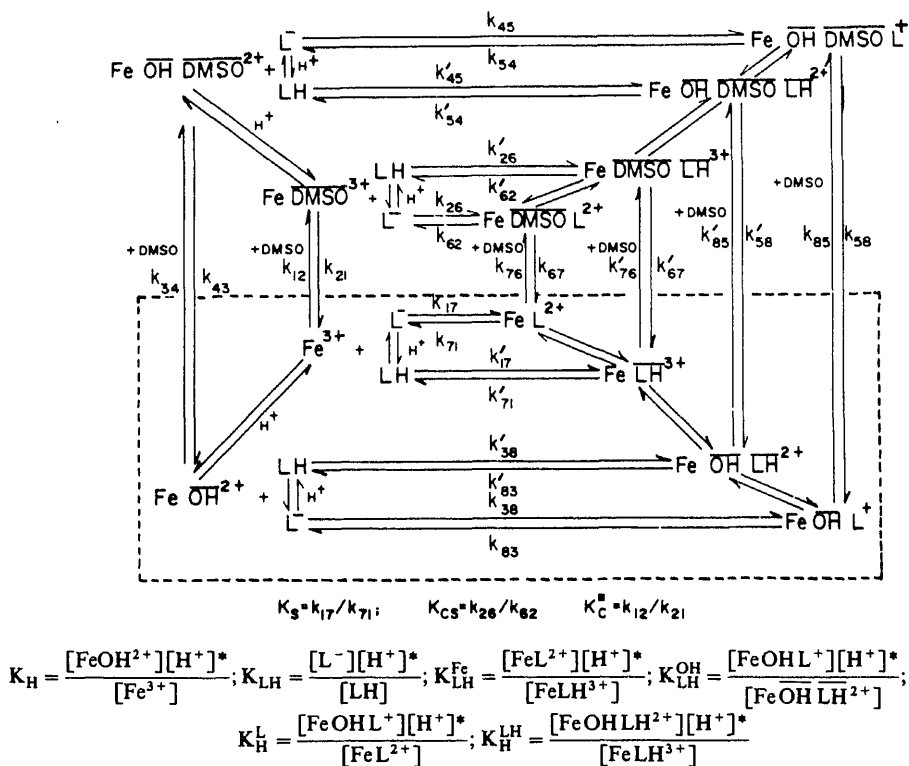


Figure 1. A reaction scheme which accounts for the kinetics of the formation of Fe(III) complexes in aqueous DMSO. Number of coordinated water molecules = 6 - number of

changes of absorbance at 350 nm with the reasonable assumption that the extinction coefficient does not change significantly with the solvent composition in H₂O-DMSO mixtures.

3.2 The formation constant K_s

The constant K_s ($= k_{17}/k_{71}$) associated with the formation of FeL^{2+} (neglecting the water molecules for simplicity) at various H₂O-DMSO mixtures are obtained from the slopes of plots of optical density (OD) vs $\text{OD}/[\text{L}^-]$. In the case of SCN^- , K_s values are given in column 4 of table 1 of our earlier work (Krishnamoorthy and Prabhananda 1981). (Terms involving K_{CS} are neglected since analysis of OD vs $\text{OD}/[\text{L}^-]$ plots show that $K_{CS} < 0.1 K_s$.) For the ligand N_3^- , values of K_{LH} and concentrations of HN_3 were used to calculate $[\text{N}_3^-]$ at different pH values. In this case (N_3^-), the slopes $1/K_s''$ obtained in various H₂O-DMSO mixtures could be fitted to the following equation

$$1/K_s'' = (1 + K_C^* \gamma [\text{DMSO}])/K_s \quad (9)$$

with $K_C^* = 3 \text{ M}^{-1}$ and $K_s = 1.67 \times 10^4 \text{ M}^{-1}$. γ is the activity coefficient of DMSO (Lam and Benoit 1974). This value of K_C^* is comparable to that determined from temperature-jump experiments (Krishnamoorthy and Prabhananda 1981). Also analysis suggests that $K_{CS} \ll K_s$.

3.3 Kinetic studies and evaluation of dominant pathways

The experimentally observed time dependence of the concentration in temperature-jump and stopped flow observation can be written as follows:

$$\frac{d}{dt} \{ [\text{FeL}^{2+}]_{\text{eq}} - [\text{FeL}^{2+}] \} = -k \{ [\text{FeL}^{2+}]_{\text{eq}} - [\text{FeL}^{2+}] \}, \quad (9)$$

where $[\text{FeL}^{2+}]_{\text{eq}}$ is the concentration at equilibrium. From the time constant associated with the exponential change, we get the relaxation rate k ($= 1/\tau$). The observed dependence of τ on $[\text{DMSO}]$ and pH can be explained in terms of equations obtained for the reaction scheme given in figure 1. For this scheme, the relaxation rate $1/\tau$ for the slowest step (9) is given by

$$\begin{aligned} 1/\tau B = & X + k_{38} K_{\text{H}}/[\text{H}^+]* + k'_{17} [\text{H}^+]*/K_{\text{LH}} \\ & + K_s \gamma [\text{DMSO}] \{ k_{85} K_{\text{H}}^{\text{L}}/[\text{H}^+]* + k'_{76} [\text{H}^+]*/K_{\text{LH}}^{\text{Fe}} \}. \end{aligned} \quad (10)$$

The fast steps are similar to those mentioned earlier (Krishnamoorthy and Prabhananda 1981).

$$X = k_{17} + k'_{38} K_{\text{H}}/K_{\text{LH}} + K_s \gamma [\text{DMSO}] \{ k_{76} + k'_{85} K_{\text{H}}^{\text{L}}/K_{\text{LH}}^{\text{OH}} \} \quad (11)$$

$$B \simeq [\text{L}^-]/\{ (1 + K_{\text{H}}/[\text{H}^+]*)(1 + K_C^* \gamma [\text{DMSO}]) \} + 1/K_s, \quad (12)$$

neglecting small terms. The origin of proton ambiguity lies in our inability to identify the dominant terms of X from a pH dependent study.

N_3^- : Table 1 gives the typical values of τ obtained in the stopped flow experiments on the formation of FeN_3^{2+} . The dependence of $1/\tau B$ on $[\text{H}^+]*$ in different solvent mixtures (figure 2) could be analysed as follows:

$$1/\tau B = X + Y[\text{H}^+]* + Y'/[\text{H}^+]*, \quad (13)$$

Table 1. Observed and calculated relaxation times τ for the stopped flow experiments on the formation of FeN_3^{2+} in aqueous DMSO at 25°C and $\mu = 1.0$, $[\text{Fe}^{2+}] = 1.0 \times 10^{-4} \text{ M}$ and $[\text{N}_3^-] + [\text{HN}_3] = 4 \times 10^{-2} \text{ M}$.

Mole fraction of DMSO $f = 0.0$			Mole fraction of DMSO $f = 0.06$		
pH	Observed ^a τ m sec	Calculated τ m sec	pH	Observed ^a τ m sec	Calculated ^b τ m sec
2.00	13.0	13.2	2.00	55.3	56.0
1.86	14.8	16.1	1.85	66.0	67.1
1.66	21.3	21.2	1.66	75.4	80.4
1.50	25.8	26.1	1.51	86.0	88.7
1.36	29.8	30.3	1.36	98.0	94.0
1.23	34.3	34.6	1.23	89.4	95.5
1.10	39.3	38.6	1.14	86.4	94.8
0.95	46.0	42.8	1.01	83.0	91.4

^a The error in the value of τ is less than 5%.

^b Calculated using the constants given in the text and considering only the terms which have been shown to be dominant in the text.

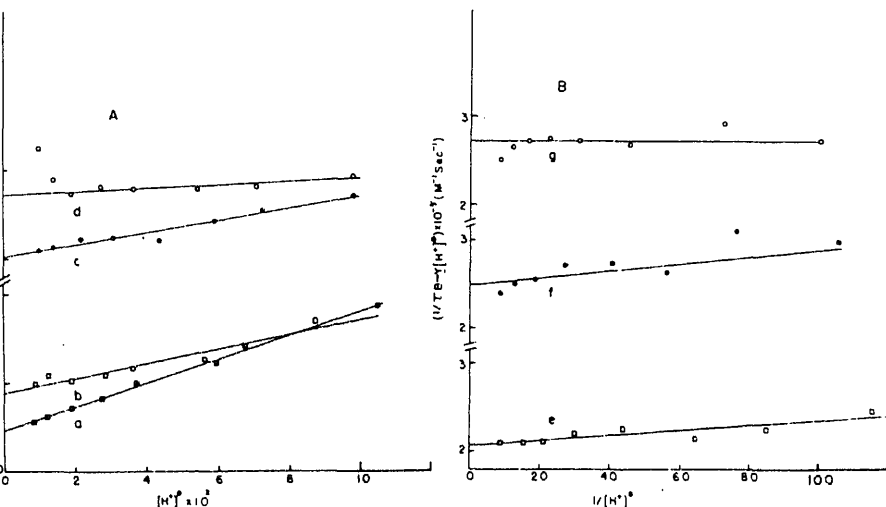


Figure 2. Dependence of $1/\tau B$ on $[\text{H}^+]^*$ in aqueous DMSO with mole fraction of DMSO $f = 0.108$ (a) 0.079 (b) 0.060 (c), 0.043 (d), 0.019 (e), 0.008 (f) and 0.0 (g) in the stopped flow experiments on the formation of FeN_3^{2+} at 25°C and $\mu = 1.0$. See text for the evaluation of Y used in plotting figure 2B.

h has the same form as (10). When the mole fraction of DMSO is large (figure 2A), the involving Y' is negligible. Table 2 gives X the pH independent part of $1/\tau B$ obtained by the least square analysis of typical data. The decrease in X with increasing

Table 2. Equilibrium and kinetic parameters for the formation of FeN_3^{2+} in DMSO-water mixtures at 25°C and $\mu = 1.0$. Calculated X and Y obtained using (14) and (15) respectively with the constants given in the text. Observed values are for a typical set of data.

Mole fraction of DMSO f	K_H/K_{LH}	$K_S\gamma[\text{DMSO}] \times 10^{-3}$	$Y \times 10^{-6} \text{ (sec}^{-1}\text{)}$		$X \times 10^{-5} \text{ (M}^{-1} \text{sec}^{-1}\text{)}$	
			Observed ^a	Calculated	Observed ^a	Calculated
0.0	42.0	0.0	—	0.056	2.72 ± 0.02 (2.54 ± 0.13) ^b	2.70
0.0079	36.2	0.423	—	0.096	2.48 ± 0.09	2.75
0.019	22.5	1.04	—	0.16	2.07 ± 0.04	2.10
0.043	10.1	2.47	0.17 ± 0.05	0.32	1.73 ± 0.03	1.39
0.060	5.8	3.58	0.68 ± 0.06	0.52	1.02 ± 0.03	1.03
0.079	3.2	4.82	0.84 ± 0.05	0.76	0.85 ± 0.02 (0.99 ± 0.03) ^b	0.76
0.108	1.2	7.15	1.34 ± 0.04	1.36	0.46 ± 0.02	0.51

^a Determined from the slopes and intercepts of figure 2. The errors given correspond to those obtained by the least square analysis of a particular set of data.

^b From the temperature jump experiments.

insensitive to the solvent composition. The analysis given below does show that the rate constants do not vary significantly with solvent composition. The values of X corresponding to seven solvent mixtures could be fitted to a linear equation with only three constants b_1 , b_2 and b_3 quite well.

$$X = b_1 K_H/K_{LH} + b_2 K_S\gamma[\text{DMSO}] + b_3 K_S\gamma[\text{DMSO}] \cdot K_H/K_{LH}. \quad (14)$$

The four values of Y (table 2) could be fitted to a linear equation with only two constants, b_4 and b_5 .

$$Y = b_4 + b_5 K_S\gamma[\text{DMSO}]/K_{LH}. \quad (15)$$

In figure 2B we have used Y extrapolated with the help of (15).

Since the number of simultaneous equations used are more than the number of terms in (14) and (15), we can have confidence that the dominant variables contributing the X and Y have been included in these equations and the rate constants b_i ($i = 1, 5$) do not vary significantly with solvent composition in aqueous DMSO. All the terms of (13)–(15) are identifiable as the dominant terms of (10) and (11) when we use the following relations:

$$\begin{aligned} b_6 K_H/K_{LH} &= K_H^L/K_{LH}^{\text{OH}} \\ b_7/K_{LH} &= 1/K_{LH}^{\text{Fe}}. \end{aligned} \quad (16)$$

This confirms that figure 1 is a reasonable scheme for our system. (Using microscopic reversibility in figure 1, we find that b_6 and b_7 can be expressed in terms of rate constants of different paths of ligand coordination to the metal and ligand dissociation from the complex.)

Using (14)–(16) and using the estimates of Seewald and Sutin (1963) for k_{17} ($= 4 \text{ M}^{-1} \text{sec}^{-1}$ at $\mu = 1.0$), we obtain by the least square analysis of data $b_1 = b_1' = 6.4 \pm 0.2 \times 10^3 \text{ M}^{-1} \text{sec}^{-1}$, $b_2 = b_2' = 2.9 \pm 1.2 \text{ M}^{-1} \text{sec}^{-1}$.

The estimate of k'_{38} obtained here agrees well with that determined by Seewald and Sutin (1963). Tables 1 and 2 include the calculated values τ , X and Y using these estimates.

Changes in the solvent composition in aqueous DMSO undoubtedly changes the free energies of the transition states as well as the reactant pair states. It is reasonable to have a situation when the difference in the free energies of a transition state and a reactant pair state does not change significantly, even though the absolute free energies change with solvent composition. In such a situation the associated bimolecular rate constant would not vary significantly with solvent composition. The constancy of bimolecular rate constants determined above could correspond to such situations.

In the limit of aqueous solutions $\{[\text{DMSO}] \rightarrow 0 \text{ in (11)–(16)}\}$ the dominant term of X is $k'_{38}K_{\text{H}}/K_{\text{LH}}$. The above conclusion regarding the constancy of k'_{38} implies that the free energy difference between the reactant pairs $\text{FeOH}^{2+} + \text{HN}_3$ and the transition state responsible for the dominant term, does not vary significantly with solvent composition in aqueous DMSO. Since the changes in the dielectric constant are small, we can neglect the changes in the electrostatic contributions to the free energy. However, changing the solvent composition in aqueous DMSO would change the solvation energies associated with the hydrogen bonding of the solvent with solute molecules, since DMSO is only a proton acceptor, whereas water can act both as a proton donor and as a proton acceptor. If there is a structural similarity between the constituents of the transition state and a reactant pair, the transition state could form hydrogen bonds with as much facility as it is possible for the reactant pair except for a small steric factor. In such a case, the free energy difference between the reactant pair stated and the transition state would not change much with solvent composition. Such an argument and the above mentioned implication of the constancy of k'_{38} suggest that the dominant transition state contributing to X is of the type $(\text{FeOH}^{2+} \cdot \text{HN}_3)$.

SCN^- : Figure 3 gives $1/\tau B$ against $1/[\text{H}^+]$ plots obtained for the ligand SCN^- in three typical solvent mixtures. Unlike the above mentioned case of N_3^- , X does not vary with solvent mixture composition in the case of the SCN^- ligand. From (11) we note that this would be the case if the dominant term of X is k_{17} . By arguments similar to the above, we can say that the dominant transition state making this contribution is $(\text{Fe}^{3+} \cdot \text{SCN}^-)$.

The equilibrium and kinetic data of this work and our earlier work (Krishnamoorthy and Prabhananda 1981) can be explained with equations which have dominant terms linear in ligand and DMSO concentrations apart from the constant terms. This suggests that we need not consider species with more than one ligand and one DMSO coordinated to the metal ion. The coordination of a second ligand is known to be much weaker than the first (Laurence 1956). In a study of chromium(III) complexes in aqueous DMSO, Scott *et al* (1969) have suggested the formation of complexes in which more than one DMSO is coordinated. Our results do not rule out the formation of such species in our system. However in the concentration range of our work, the kinetic and equilibrium results are adequately explained by the species shown in figure 1.

The dependence of various parameters on solvent composition in aqueous DMSO observed in this work has similarities with that reported earlier (Krishnamoorthy and Prabhananda 1981; Buncel and Wilson 1977). It is also gratifying to note that our identification of the dominant transition states are in accordance with the expectations

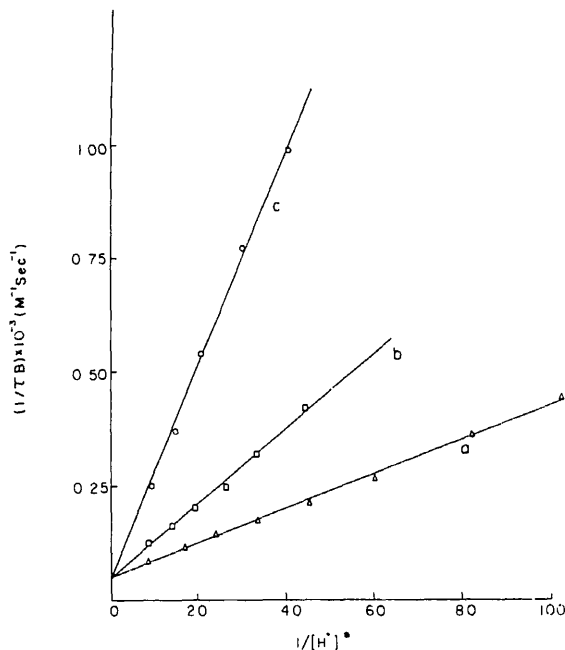


Figure 3. Dependence of $1/\tau B$ on $[H^+]*$ in aqueous DMSO with mole fraction of DMSO $f = 0.079$ (a), 0.043 (b) and 0.0 (c) in the stopped flow experiments on the formation of $FeSCN^{2+}$ at $25^\circ C$ and $\mu = 1.0$.

1965). We note that we cannot neglect species of the type $FeOH \cdot N_3^+$, $FeOH \cdot HN_3^{2+}$, $FeHN_3^{3+}$ and the DMSO coordinated species while accounting for the kinetic behaviour.

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Preparation, characterization and thermal analysis of metal hydrazinocarboxylate derivatives

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Abstract. The reaction of hydrazinocarboxylic acid, N_2H_3COOH , with metal ions in the presence of hydrazine hydrate yields metal hydrazinocarboxylate derivatives like: $M(N_2H_3COO)_2 \cdot nH_2O$, $M = Mg, Ca$ and Mn ; $M(N_2H_3COO)_2(N_2H_4)_2$, $M = Mn, Fe, Co, Ni$ and Zn ; $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$, $M = Fe, Co, Ni, Zn$; and $N_2H_5Mg(N_2H_3COO)_3$. Reaction conditions to obtain a desired product have been standardised and a probable reaction mechanism for the formation of different products proposed. Thermal analysis of the compounds has been investigated using simultaneous TG-DTG-DTA. Metal hydrazinocarboxylate derivatives decompose in air at low temperatures to the respective metal oxides.

Keywords. Metal hydrazinocarboxylates; infrared spectra; thermal analysis.

Introduction

Transition metal ions are known to react with hydrazine hydrate saturated with carbon dioxide to yield metal hydrazinocarboxylate derivatives like $M(N_2H_3COO)_2 \cdot nH_2O$, $M(N_2H_3COO)_2(N_2H_4)_2$ or $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$. Hydrazinocarboxylic acid, N_2H_3COOH formed metathetically by the reaction of CO_2 with N_2H_4 appears to react with the metal ions to form these complexes. Ferrari *et al* (1965) and Braibanti *et al* (1966, 1967a, b, 1968, 1971) have reported the preparation, IR spectra and crystal structures of a number of these complexes. They have shown that the hydrazinocarboxylate anion, $N_2H_3COO^-$ acts as a bidentate group coordinating the metal through both N and O atoms. Thermal decomposition of some metal hydrazinocarboxylate complexes has been studied and reported to yield finely divided metals or metal oxides (Macek *et al* 1976).

During the course of our studies on hydrazine derivatives we have reported the preparation and thermal properties of some metal hydrazinocarboxylate derivatives (Patil *et al* 1979a, b, 1983). They were prepared both by homogeneous and heterogeneous reactions. However, the exact reaction conditions to obtain a desired product do not appear to have been standardised. Present study is, therefore, aimed at standardising

2. Experimental

Hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) 99–100%, BDH, was used in all the reactions.

2.1 Preparation of hydrazinocarboxylic acid, $\text{N}_2\text{H}_3\text{COOH}$

(a) Hydrazine hydrate was saturated with carbon dioxide at room temperature until a white precipitate separated. The precipitate was dried and stored over P_2O_5 in a vacuum desiccator.

(b) Dissolution of 25 g of ammonium carbonate in 50 ml of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gave a viscous liquid ($\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$). Passing $\text{CO}_2(g)$ through this resulted in the formation of a white solid which was dried and stored over P_2O_5 in a vacuum desiccator.

The chemical analysis and IR spectrum of the white solid correspond to that of $\text{N}_2\text{H}_3\text{COOH}$. A 5% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was used in the preparation of metal hydrazinocarboxylate hydrates and hydrazinates. In the case of hydrazinium derivatives a 15% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was employed.

2.2 Preparation of metal hydrazinocarboxylate hydrates and hydrazinates

An aqueous solution containing metal ions like Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} or Zn^{2+} (25 ml, 0.4 M) was treated with a 5% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ until the precipitate formed initially just dissolved. The clear solution thus obtained was kept open to the atmosphere. Crystalline solids separated from the solution within a couple of days. The composition of the crystals was fixed by chemical analysis to be $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M} = \text{Mg, Ca and Mn}$; and $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$, $\text{M} = \text{Mn, Fe, Co, Ni and Zn}$ (table 1). Manganese hydrazinocarboxylate hydrazinate, $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2 (\text{N}_2\text{H}_4)_2$ was obtained by treating a fine powder of $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

2.3 Preparation of hydrazinium metal hydrazinocarboxylate derivatives

An aqueous solution containing metal ions like Fe^{2+} , Co^{2+} , Ni^{2+} or Zn^{2+} (25 ml, 0.4 M) was treated with a 15% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ until the precipitate formed initially just dissolved. The resulting clear solution was left open to atmosphere. Beautiful crystals separated from the solution in 3–4 days. The composition of the crystals was fixed by chemical analysis to be $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$, $\text{M} = \text{Fe, Co, Ni and Zn}$ (table 1).

Hydrazinium magnesium hydrazinocarboxylate, $\text{N}_2\text{H}_5\text{Mg}(\text{N}_2\text{H}_3\text{COO})_3$ was obtained by dissolving magnesium powder in the 15% solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. The complex was precipitated by the addition of alcohol.

2.4 Analysis

The metal content in the complexes were determined by EDTA complexometric titration. Hydrazine content was estimated volumetrically using 0.025 M KIO_3 solution under Andrews' conditions (Vogel 1961).

Table 1. Chemical analysis of metal hydrazinocarboxylate derivatives.

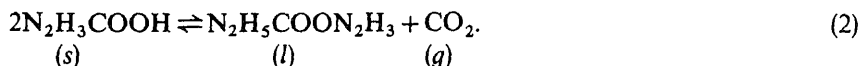
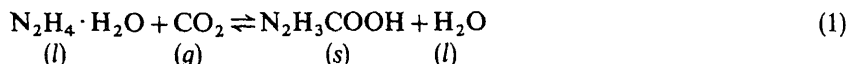
Compound	% of Metal		% of Hydrazine	
	Observed	Required	Observed	Required
Mg(N ₂ H ₃ COO) ₂ (H ₂ O) ₂	11.44	11.55	30.24	30.43
Ca(N ₂ H ₃ COO) ₂ H ₂ O	19.12	19.26	30.64	30.75
Mn(N ₂ H ₃ COO) ₂ (H ₂ O) ₂	22.75	22.80	26.46	26.56
Mn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	20.22	20.42	47.32	47.59
Fe(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	20.70	20.69	47.50	47.47
Co(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	21.60	21.58	46.40	46.89
Ni(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	21.48	21.52	46.23	46.93
Zn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	23.23	23.39	45.38	45.81
N ₂ H ₅ Mg(N ₂ H ₃ COO) ₃	7.99	8.01	43.00	42.62
N ₂ H ₅ Fe(N ₂ H ₃ COO) ₃ · H ₂ O	16.32	16.82	38.64	38.57
N ₂ H ₅ Co(N ₂ H ₃ COO) ₃ · H ₂ O	17.48	17.59	38.11	38.21
N ₂ H ₅ Ni(N ₂ H ₃ COO) ₃ · H ₂ O	17.50	17.58	38.20	38.28
N ₂ H ₅ Zn(N ₂ H ₃ COO) ₃ · H ₂ O	19.08	19.14	37.56	37.49

TGD-5000 RH. thermobalance of ULVAC-RIKO, Japan. All the experiments were carried out using 4–5 mg samples under ambient conditions. The heating rate employed was 20°C/min. The decomposition/combustion residues of the complexes were characterized by x-ray powder diffraction patterns recorded on a Philips pw 1050/70 diffractometer using CuK α and CoK α radiation.

3. Results and discussion

3.1 Hydrazinocarboxylic acid, N₂H₃COOH

Stolle and Hoffman (1904) have reported the formation of hydrazinocarboxylic acid, N₂H₃COOH by passing a current of CO₂ through a well cooled solution of hydrazine. The acid, N₂H₃COOH, was reported to decompose partially with the evolution of CO₂ when heated (~ 90°C) to give a viscous liquid whose composition was not exactly known. Presently, we were able to prepare N₂H₃COOH not only by passing a current of CO₂ through N₂H₄ · H₂O at room temperature but also by the reaction of CO₂ with N₂H₅COON₂H₃ prepared by dissolving ammonium carbonate in N₂H₄ · H₂O (Patil *et al* 1979b). Thus the following equilibrium appears to exist in the N₂H₄ · H₂O-CO₂ reaction.



Hydrazinocarboxylic acid (carbazic acid) is highly hygroscopic and should be stored over P₂O₅ or H₂SO₄ in a vacuum desiccator. It dissolves in water with dissociation as shown in (1). The acid was characterized by chemical analysis (% N₂H₄-observed

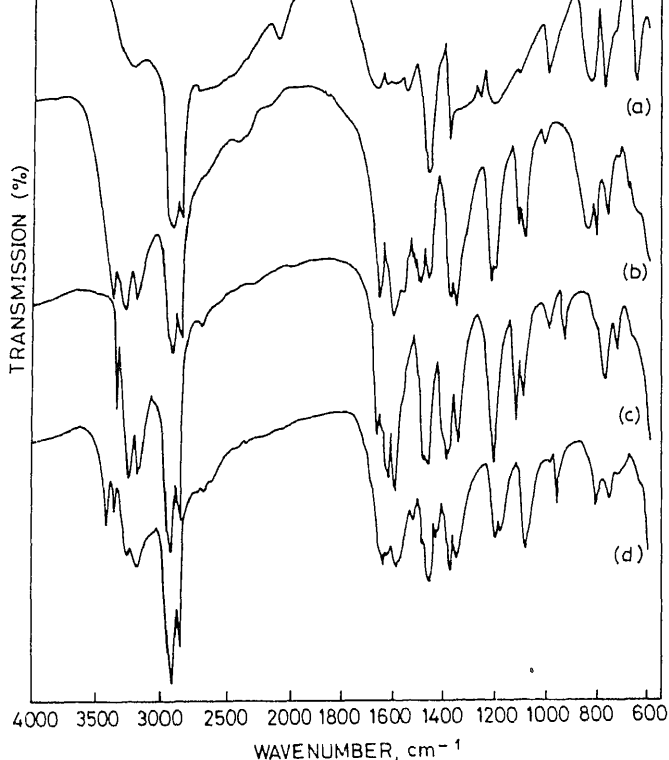


Figure 1. Infrared absorption spectra of (a) $\text{N}_2\text{H}_3\text{COOH}$, (b) $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$, (c) $\text{Co}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$, (d) $\text{N}_2\text{H}_3\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$.

640 cm^{-1} . The TG-DTG-DTA curve of $\text{N}_2\text{H}_3\text{COOH}$ (figure 2) shows a two-step decomposition. The first step with a weight loss of 15 % could be attributed to the partial decomposition of $\text{N}_2\text{H}_3\text{COOH}$ to $\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$ with the evolution of CO_2 as in (2). The corresponding reaction in DTA is seen as a broad endotherm at 107°C probably due to the combination of melting and decomposition. In the second step (100% weight loss) the resulting viscous liquid $\text{N}_2\text{H}_5\text{COON}_2\text{H}_3$ volatilizes with decomposition.

3.2 Mechanism

The reaction of metal ions with $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gave $\text{M}(\text{N}_2\text{H}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$, $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$ and/or $\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ type complexes. It is interesting to note that dilute solutions of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ gave either hydrates or hydrazinates and concentrated solutions (15 %) gave hydrazinium complexes. Since the solution of $\text{N}_2\text{H}_3\text{COOH}$ in $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ essentially contains N_2H_5^+ , $\text{N}_2\text{H}_3\text{COO}^-$, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and H^+ species, one can write the following stoichiometric reactions for the various complexes formed.

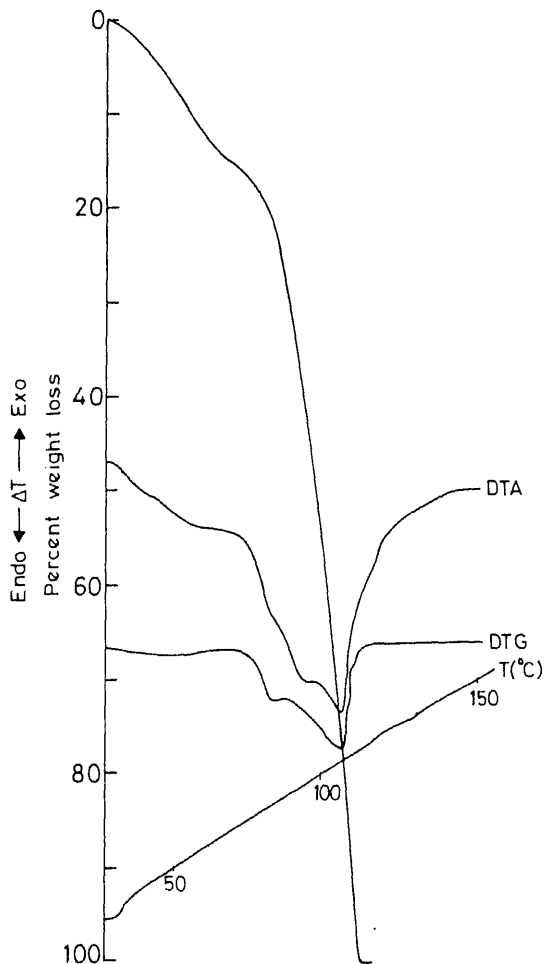
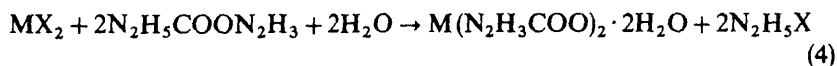
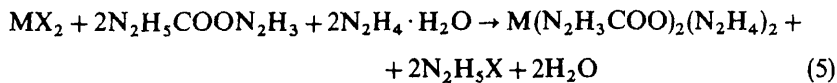


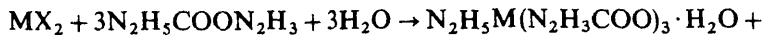
Figure 2. Simultaneous TG-DTG-DTA of $\text{N}_2\text{H}_3\text{COOH}$.



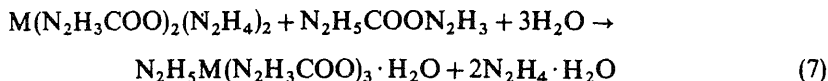
M = Mg, Ca and Mn.



M = Fe, Co, Ni and Zn.



either $M(N_2H_3COO)_2 \cdot 2H_2O$ or $M(N_2H_3COO)_2(N_2H_4)_2$. Only transition metal ions appear to form both hydrazinate and hydrazinium complexes. Hydrazinate complexes initially formed appear to react with excess of ligand (in concentrated solutions) to yield the corresponding hydrazinium salts as shown below:



This fact was confirmed by treating hydrazinate complexes with the ligand. However, manganese does not form $N_2H_5Mn(N_2H_3COO)_3 \cdot H_2O$. The calcium salt appears to be unique in that it forms only monohydrate, $Ca(N_2H_3COO)_2 \cdot H_2O$ whereas magnesium forms $N_2H_5Mg(N_2H_3COO)_3$ by the dissolution of the metal.

3.3 Infrared spectra

Infrared spectra of metal hydrazinocarboxylates have been studied and important IR absorption frequencies assigned (Patil *et al* 1983; Braibanti *et al* 1968). Typical IR spectra of $M(N_2H_3COO)_2 \cdot 2H_2O$, $M(N_2H_3COO)_2(N_2H_4)_2$ and $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$ are shown in figure 1. As mentioned earlier, the $N_2H_3COO^-$ group acts as a bidentate ligand and coordinates to the metal through both the N and the O atoms forming a 5-membered ring. The characteristic N-N stretching frequency of bidentate $N_2H_3COO^-$ is seen in the region $990-1015\text{ cm}^{-1}$ in all the complexes. The metal ions in all these complexes have octahedral coordination. The octahedra is completed by the two water molecules in $M(N_2H_3COO)_2 \cdot 2H_2O$; and by the two monodentate N_2H_4 groups in $M(N_2H_3COO)_2(N_2H_4)_2$. Infrared spectra of the hydrazinates clearly show ν_{N-N} of monodentate $N_2H_4 \sim 925\text{ cm}^{-1}$ in addition to ν_{N-N} of $N_2H_3COO^- \sim 1000\text{ cm}^{-1}$. In the case of hydrazinium complexes, $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$ the octahedra around the metal atom involve 3 bidentate $N_2H_3COO^-$ groups, neither $N_2H_5^+$ nor H_2O is coordinated to the metal. The characteristic IR frequency of ionic $N_2H_5^+$ is seen $\sim 965\text{ cm}^{-1}$ in all these complexes.

3.4 Thermal analysis

The results of TG-DTG-DTA of $M(N_2H_3COO)_2 \cdot nH_2O$, $M(N_2H_3COO)_2(N_2H_4)_2$ and $N_2H_5M(N_2H_3COO)_3 \cdot H_2O$ are summarized in tables 2, 3 and 4 respectively. Some representative thermograms are shown in figure 3-5.

3.4a Metal hydrazinocarboxylate hydrates: All the metal hydrazinocarboxylate hydrates [$M(N_2H_3COO)_2 \cdot nH_2O$, $M = Mg, Ca$ and Mn] lose the water of hydration initially to yield the corresponding metal hydrazinocarboxylates. The dehydration takes place at fairly high temperature ($100-200^\circ\text{C}$) indicating the presence of coordinated water molecules. The anhydrous metal hydrazinocarboxylates decompose exothermically to yield the corresponding metal oxides. The decomposition of the calcium salt shows 4 distinct steps corresponding to the formation of $Ca(N_2H_3COO)_2$, CaC_2O_4 , $CaCO_3$ and CaO respectively. Based on this observation and our early study (Patil *et al* 1979b) the intermediates in the decomposition of both $Mg(N_2H_3COO)_2$ and $Mn(N_2H_3COO)_2$ could be the corresponding metal oxalates. The composition of

Table 2. Thermal analysis of metal hydrazinocarboxylate hydrate.

Thermogravimetry						
Compound	DTA peak temperature (°C)	Step no.	Temperature range (°C)	Total weight loss (%)		Products
				Observed	Required	
$\text{Mg}(\text{N}_2\text{H}_5\text{COO})_2(\text{H}_2\text{O})_2$	170 (endo)	1	150-180	18.00	17.11	$\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2$
	325 (exo) }	2	180-485	81.00	80.83	MgO
	380 (exo) }					
	135 (endo)	1	115-152	8.60	8.65	$\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2$
$\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2\text{H}_2\text{O}$	281 (exo) }	2	152-310	38.20	38.44	CaC_2O_4
	308 (exo) }					
	345 (exo) }	3	310-700	51.80	51.90	CaCO_3
	420 (exo) }	4	700-930	73.00	73.04	CaO
$\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$	720 (endo)	1	110-170	15.80	14.94	$\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2$
	130 (endo)	2	170-205	29.50	27.39	$\text{MnC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$
	170 (exo) 180 (exo)					
	200 (exo)	3	205-300	69.90	70.55	MnO

Table 3. Thermal data of metal hydrazinocarboxylate hydrazinates.

Thermogravimetry						
Compound	DTA peak temperature (°C)	Step no.	Temperature range (°C)	Total weight loss (%)		Products
				Observed	Required	
Mn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	175 (exo) } 195 (exo) }	1	130-290	72.80	73.68	MnO
Fe(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	135 (exo) } 175 (exo) }	1	130-205	70.10	70.41	Fe ₂ O ₃
Co(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	190 (exo) } 200 (exo) }	1	210-269	70.00	70.59	Co ₃ O ₄
Ni(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	195 (exo) } 228 (exo) }	1	187-200	72.00	72.60	NiO
Zn(N ₂ H ₃ COO) ₂ (N ₂ H ₄) ₂	200 (exo)	1	155-250	32.00	33.64	ZnC ₂ O ₄ · N ₂ H ₄
	310 (exo)	2	250-325	71.90	70.87	ZnO

Table 4. Thermal analysis of hydrazinium metal hydrazinocarboxylates.

Thermogravimetry						
Compound	DTA peak temperature (°C)	Step No.	Temperature range (°C)	Total weight loss (%)		Products
				Observed	Required	
$N_2H_3Fe(N_2H_3COO)_3 \cdot H_2O$	165 (exo) }	1	145-220	76.00	75.93	Fe_2O_3
	180 (exo) }					
$N_2H_3Co(N_2H_3COO)_3 \cdot H_2O$	175 (exo)	1	170-245	36.50	37.61	$CoC_2O_4 \cdot 2N_2H_4$
	245 (exo)	2	245-280	76.10	76.03	CO_3O_4
$N_2H_3Ni(N_2H_3COO)_3 \cdot H_2O$	182 (exo)	1	170-210	48.00	46.60	$NiC_2O_4 \cdot N_2H_4$
	193 (exo) }	2	210-385	76.00	77.67	NiO
	220 (exo) }					
$N_2H_3Zn(N_2H_3COO)_3 \cdot H_2O$	145 (endo)	1	70-165	18.00	18.16	$Zn(N_2H_3COO)_2(N_2H_4)$
	195 (exo)	2	165-215	53.00	55.07	ZnC_2O_4
	240 (exo)	3	215-390	76.00	76.17	ZnO
	120 (endo)	1	50-135	36.00	37.52	$MgC_2O_4 \cdot 2N_2H_4$
$N_2H_3Mg(N_2H_3COO)_3$	320 (exo)	2	135-343	72.20	70.13	$MgCO_3$
	390 (endo)	3	343-418	86.00	85.72	MgO

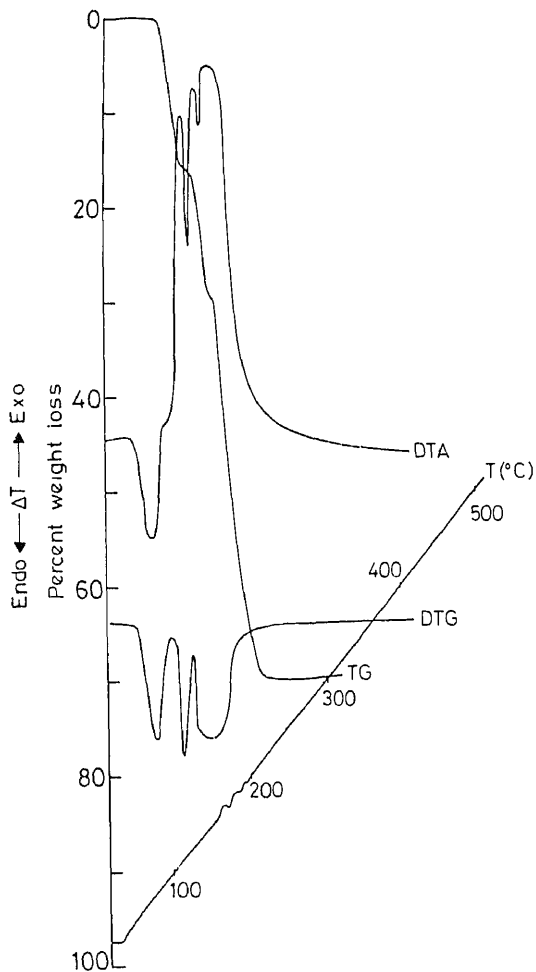


Figure 3. Simultaneous TG-DTG-DTA of $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2(\text{H}_2\text{O})_2$.

the final metal oxides was fixed by the observed weight loss in TG and their characteristic x-ray powder diffraction patterns.

3.4b Metal hydrazinocarboxylate hydrazinates: All the hydrazinate complexes $[\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2]$, $\text{M} = \text{Mn, Fe, Co, Ni}$ and Zn] except zinc show single step decomposition in TG-DTG. However, DTA shows two exotherms probably corresponding to the decomposition of coordinated hydrazine followed by the decomposition of metal hydrazinocarboxylates to the respective metal oxides. The zinc complex appears to decompose through $\text{ZnC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$. The decomposition products (metal oxides) were identified by their x-ray powder diffraction patterns.

3.4c Hydrazinium metal hydrazinocarboxylate derivatives: Thermal decomposition of these complexes $[\text{N}_2\text{H}_5\text{M}(\text{N}_2\text{H}_2\text{COO})_3 \cdot \text{H}_2\text{O}]$, $\text{M} = \text{Fe, Co, Ni}$ and Zn , and

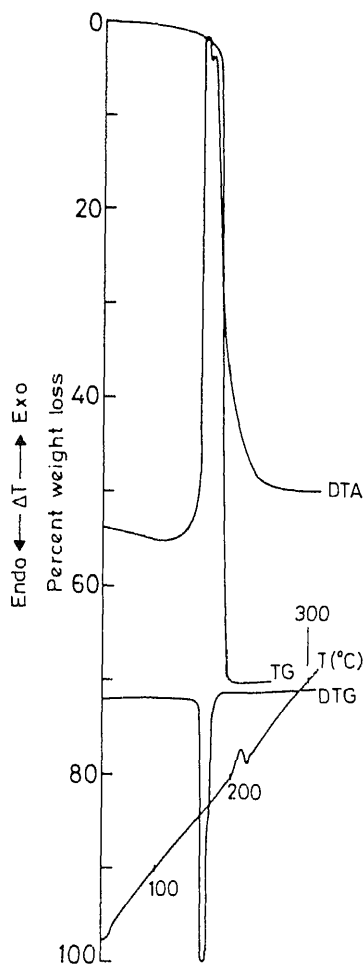


Figure 4. Simultaneous TG-DTG-DTA of $\text{Co}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$.

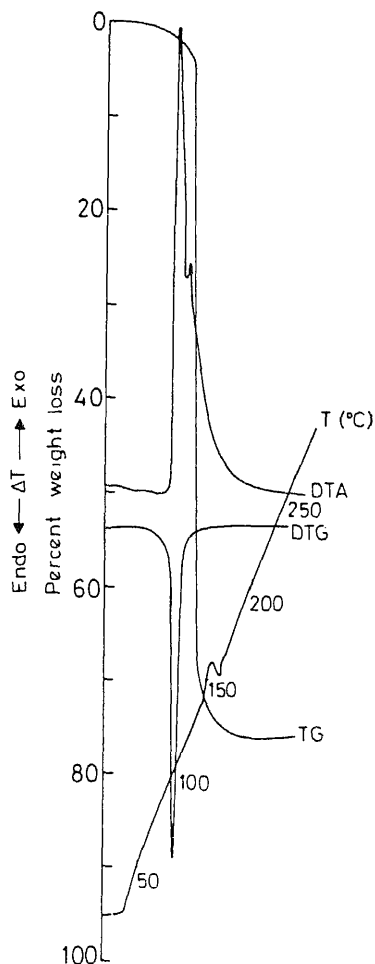


Figure 5. Simultaneous TG-DTG-DTA of $\text{N}_2\text{H}_5\text{Fe}(\text{N}_2\text{H}_3\text{COO})_3 \cdot \text{H}_2\text{O}$.

decomposition in TG-DTG and two exotherms in DTA. The observed weight loss after the first step corresponds to the formation corresponding to the metal oxalate hydrazinate, $\text{MC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$ intermediate. The decomposition of zinc and magnesium complexes involve 3-steps each. Possible intermediates could be $\text{M}(\text{N}_2\text{H}_3\text{COO})_2(\text{N}_2\text{H}_4)_2$, $\text{MC}_2\text{O}_4 \cdot \text{N}_2\text{H}_4$, MC_2O_4 , etc. Final residues of decomposition corresponds to the respective metal oxides as confirmed by x-ray powder diffraction patterns.

- (i) None of the metal ions studied form all the three types of hydrazinocarboxylate derivatives.
- (ii) Transition metal ions form hydrazinate $[M(N_2H_3COO)_2(N_2H_4)_2]$ and hydrazinium $[N_2H_5M(N_2H_3COO)_3 \cdot H_2O]$ complexes. Though manganese forms the hydrazinate it does not form the hydrazinium complex.
- (iii) Magnesium, calcium and manganese hydrazinocarboxylates form hydrated complexes. Only $Mn(N_2H_3COO)_2 \cdot 2H_2O$ when treated with $N_2H_4 \cdot H_2O$ yields the corresponding hydrazinate, $Mn(N_2H_3COO)_2(N_2H_4)_2$. Magnesium, however, gave anhydrous hydrazinium hydrazinocarboxylate, $N_2H_5Mg(N_2H_3COO)_3$.
- (iv) Transition metal hydrazinocarboxylate derivatives decompose in air at low temperature (100–200°C) to the respective metal oxides.

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Chemical synthesis of d(G-C)₄, d(G-C)₅ and d(GGTGGACCTC) by continuous flow solid phase phosphotriester method

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Abstract. A simplified protocol for the synthesis of oligodeoxyribonucleotides by phosphotriester approach on controlled pore glass resins using a manual DNA synthesiser is presented. The main features of this method are: (i) a single system of solvents (acetonitrile: dichloromethane, 8:2) is used in the assembly procedure reducing the number of mechanical manipulations, (ii) dichloroacetic acid is used as a good compromise between the efficiency of deprotection and minimal depurination and (iii) it competes effectively with the phosphite method in terms of speed, efficiency and ease. All the required protected mononucleotides and functionalised resins were home-made and detailed procedures are reported. The utility of the procedure is demonstrated by the actual synthesis of sequences d(G-C)₄, d(G-C)₅ and d(GGTGGACCTC) required for biophysical studies in our laboratory. The oligonucleotides were purified by the recently introduced method of fast protein liquid chromatography which gives good resolutions in shorter time periods as compared to the high performance liquid chromatography technique.

Keywords. Oligodeoxyribonucleotide synthesis: solid phase; fast protein liquid chromatography.

1. Introduction

The technique of solid phase synthesis has now become a versatile method for routine chemical synthesis of oligodeoxyribonucleotides (Gassen and Lang 1982; Gait 1984). This success is mainly due to constant improvements in the properties of solid supports, the efficiency of condensing agents and the amenability of the method for either partial or complete automation. Automation is achieved by a continuous-flow process in which the support is sequentially treated with the coupling mixture, solvents and the deprotecting agent for pre-determined time intervals. In such a set-up, the concentrations of the monomers typically used are about 4–5 equivalents over the resin loading and the volumes of solvents and reagents are about 10 times the bed volume for each washing. These aspects of continuous-flow synthesis amplify the effect of impurities present even in trace amounts and hence demand the use of very high purity solvents, monomers and reagents for good results. Taking these factors into consideration, one of us (Ganesh 1984) recently presented a simplified protocol for the synthesis of oligodeoxynucleotides by a continuous-flow phosphotriester approach on controlled pore glass resins. One of the features of this method is that all the required monomers were prepared in our laboratory starting from deoxynucleosides using

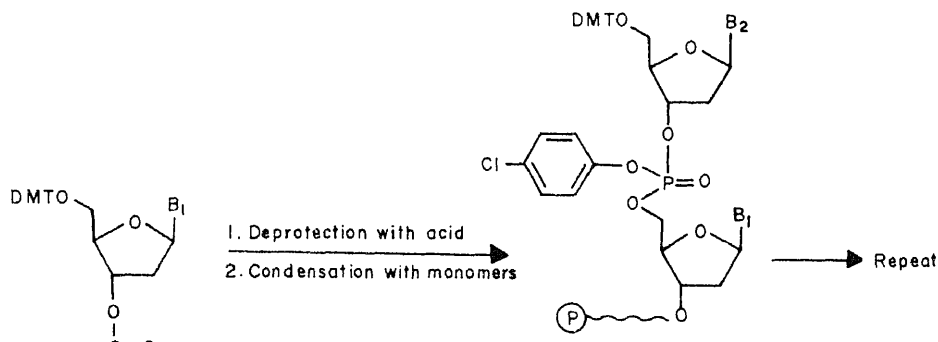
indigenous reagents and solvents. In this paper, we present the detailed methodology for the synthesis of monomers, functionalisation of resins and the application of the reported method for the successful synthesis of DNA fragments $d(G-C)_4$, $d(G-C)_5$ and $d(GGTGGACCTC)$.

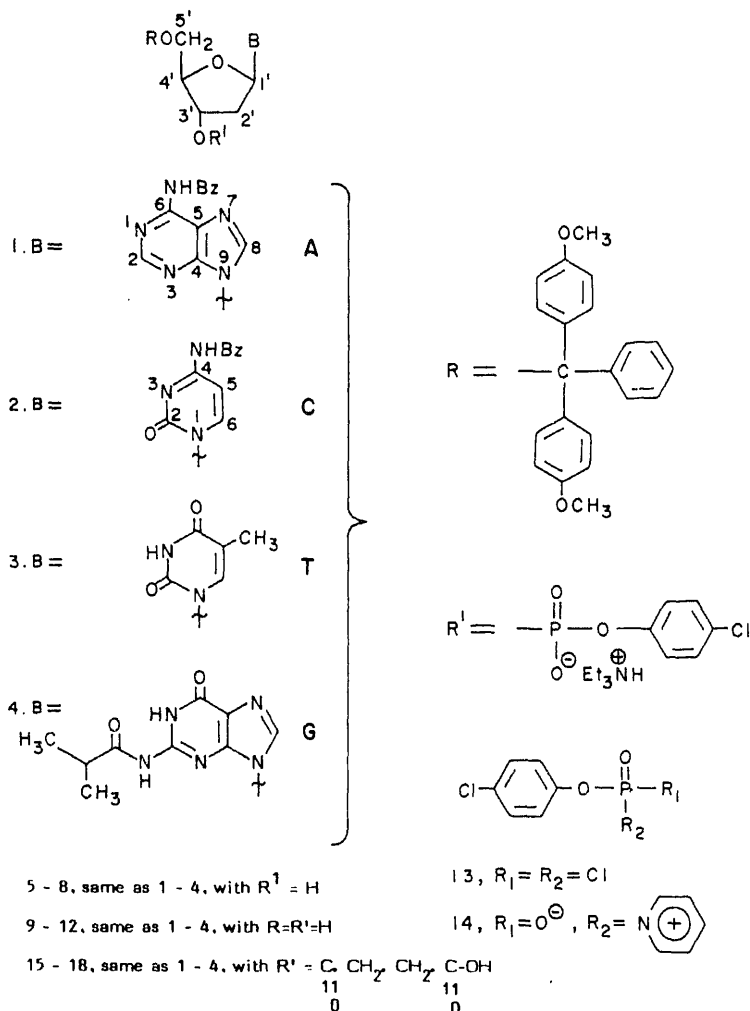
2. Results and discussion

2.1 Preparation of the monomers

The monomers required for the solid phase synthesis (scheme 1) are the protected deoxynucleotides (1–4, scheme 2) derived from the protected nucleosides (5–8). The latter were prepared by the one-pot transient protection method of Ti *et al* (1982). The unprotected deoxynucleosides (dA, dC and dG) were first treated with trimethylchlorosilane in pyridine to mask the hydroxyl groups, immediately followed by reaction with benzoyl chloride (for dA and dC) and isobutyryl chloride (for dG) to obtain N-acyl-3,5-bis trimethylsilyl deoxynucleosides. The hydrolysis of the silyl groups was then effected in a few minutes with aqueous ammonia to obtain the N-acyl-2'-deoxynucleosides (9–12) in 85–90% yields. These were converted into respective N-acyl-5'-O-(4,4'-dimethoxytrityl)-2'-deoxynucleosides (5–8) by treatment with 4,4'-dimethoxytrityl chloride in pyridine and the products were purified by flash chromatography on silica gel H. This one-flask procedure of preparing the N-acyl-5'-O-protected nucleosides is less cumbersome and much quicker than conventional methods (Narang *et al* 1980).

The N,O-protected deoxynucleosides (5–8) were phosphorylated at the 3'-hydroxyl group by the procedure of Effimov *et al* (1982). Here the phosphorylating agent is the reactive 4-chlorophenyl phosphoryl pyridinium derivative (14) which is generated *in situ* by simple addition of an equimolar amount of water to 4-chlorophenyl phosphorodichloridate (13) in pyridine. The latter reagent was prepared by reaction of 4-chlorophenol with phosphorous oxychloride (Owen *et al* 1974) and purified by





Scheme 2.

vacuum distillation. This procedure of phosphorylation of nucleosides is more convenient as compared to the use of bifunctional phosphorylating agents such as tri- or tetraazole activated 4-chlorophenyl phosphates (Narang *et al* 1980) and the yields of phosphodiester isolated as triethylammonium salts (1-4) are satisfactory. These crude nucleotide monomers were purified on a short column of silica gel H under a nitrogen atmosphere and were homogeneous on silica gel TLC plates as detected by UV and trityl positive spots.

2.2 Functionalisation of the resin

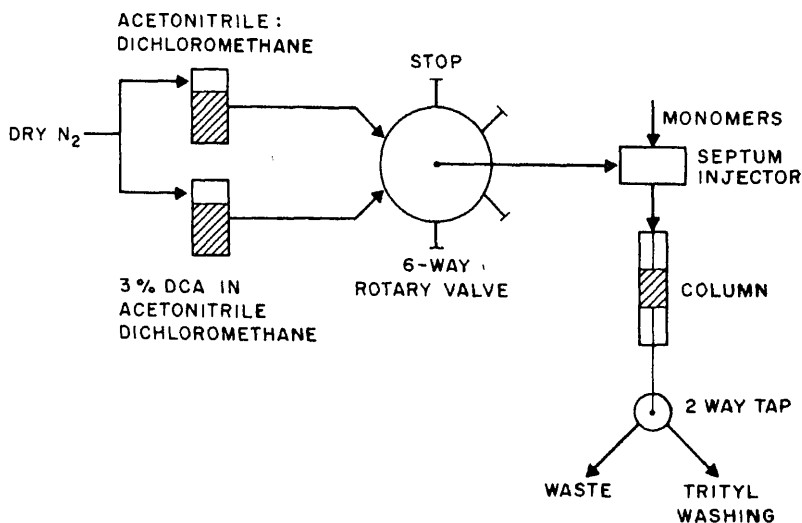
The controlled pore glass resin supplied by Pierce already carries a long chain alkyl

cedure (Gait *et al* 1982). The latter were prepared by the reaction of N-acyl-5'-O-dimethoxytrityl deoxynucleosides (5-8) with succinic anhydride and 4-dimethylaminopyridine in pyridine. The symmetrical anhydride of the 3'-O-succinyl nucleosides was obtained using DCC as the condensing agent and the functionalisation of the resin was smooth in dimethylformamide. The resin (9), functionalised by linking to the first nucleoside through 3'-hydroxyl, was finally capped by acetylation to block the remaining free amino groups and at this stage the resin showed a negative test with ninhydrin test solutions (Kaiser *et al* 1970). The nucleoside loadings on the resins as estimated by trityl analyses of the resins after treatment with 60% perchloric acid-ethanol were about 30-35 μ mole g^{-1} .

2.3 Assembly and deprotection of the oligonucleotide chains

Oligonucleotides were synthesised on the functionalised support in the 3' to 5' direction by a cyclical method involving only two chemical reactions per cycle (scheme 1). The first consists of the removal of the 5'-O-trityl protecting group by a suitable protic acid, followed by solvent washing to remove residual acid on the resin. During the second reaction, the appropriate nucleotide monomer (1-4) in the form of triethylammonium salts is condensed with the acid liberated 5'-hydroxyl groups on the resin in presence of an activating agent and a nucleophilic catalyst. These reactions are easily manipulated with an OMNIFIT manual DNA synthesiser by the continuous-flow method (Gait *et al* 1980, figure 1). The resin is contained in a small glass column fitted with a 6-way rotary valve which allows the selection of solvents and reagents flowing through the column. The coupling mixture consisting of the monomer, the condensing agent and the catalyst is injected into the column at appropriate points during the cycle through a septum fitted onto its top.

Based on the idea suggested by Effimov *et al* (1982), we have used a single solvent system acetonitrile : dichloromethane (8 : 2 v/v) for washing the resin, the condensations



being carried out in acetonitrile. This is a very convenient solvent system as compared to pyridine used in other phosphotriester approaches (Sproat and Bannworth 1983) because of its ease of purification and its being less unpleasant to work with. The efficiency of condensation in acetonitrile is as good and in fact slightly faster than that in pyridine. We have used a mixture of triisopropylbenzene sulphonyl chloride and N-methyl imidazole as the coupling agent and the kinetic studies of Effimov *et al* (1982) have indicated that the condensation reaction on the resin with these reagents is almost complete in 15 min. The capping reaction at the end of every monomer addition was found to be unnecessary. The detritylating agent was a 3% solution of dichloroacetic acid in acetonitrile: dichloromethane and the deprotections were essentially over within 5 min for A, T and G additions whereas with C it was a little longer. Dichloroacetic acid is found to be a better agent, than either trifluoro or trichloroacetic acids as this effects less depurinations (Adams *et al* 1983). All the acid washings were diluted to a known volume with 60% perchloric acid-ethanol and estimated spectrophotometrically by monitoring the absorbance at 495 nm. These analyses showed only a 2-3% drop in trityl values with consecutive couplings. Though this is not direct evidence of a successful synthesis, it does indicate a negligible cleavage of oligonucleotide chains from the resin during the synthesis. After the last coupling step, the trityl group was retained on the 5'-terminal nucleotide.

At the end of the assembly, the resin was treated with the oximate reagent (Reese and Zard 1981) which consists of a mixture of 2-nitrobenzaldehyde and 1,1,3,3-tetramethylguanidine in dioxane: water (1:1, v/v). This cleaves the oligonucleotides from the resin with the simultaneous deprotection of the phosphate moiety. The product was then treated with concentrated ammonia in a sealed tube at 60°C for 20 hrs to deacylate the side chain amido groups on base residues. After removal of excess ammonia, the product was reacted with 80% aqueous acetic acid for 30 min to detritylate the 5'-terminal nucleotide.

2.4 Purification of oligonucleotides

The initial purification of crude mixtures of synthetic oligonucleotides is best carried out by ion-exchange HPLC (high performance liquid chromatography) which separates oligonucleotides principally on the basis of their length. The most likely impurities in solid phase synthesis are either truncated or failure sequences which being shorter in lengths are eluted earlier and the identification of the desired peak on chromatogram is easy since it elutes as a large peak at the end. We have used the recent technique of FPLC (fast protein liquid chromatography) to purify the oligonucleotide mixtures. Compared to HPLC, this technique offers higher resolution in shorter times and preparative runs are possible with sample loads of a few milligrams. Using polyanion Si columns (Pharmacia) and phosphate buffer gradient (see experimental for details) excellent separations of oligonucleotides were obtained (figure 2). The broad peaks observed in low intensities beyond the desired product peak may arise either from the incompletely deprotected components or from the presence of secondary structures. The latter may result from the fact that the eluting conditions are not completely denaturing and the

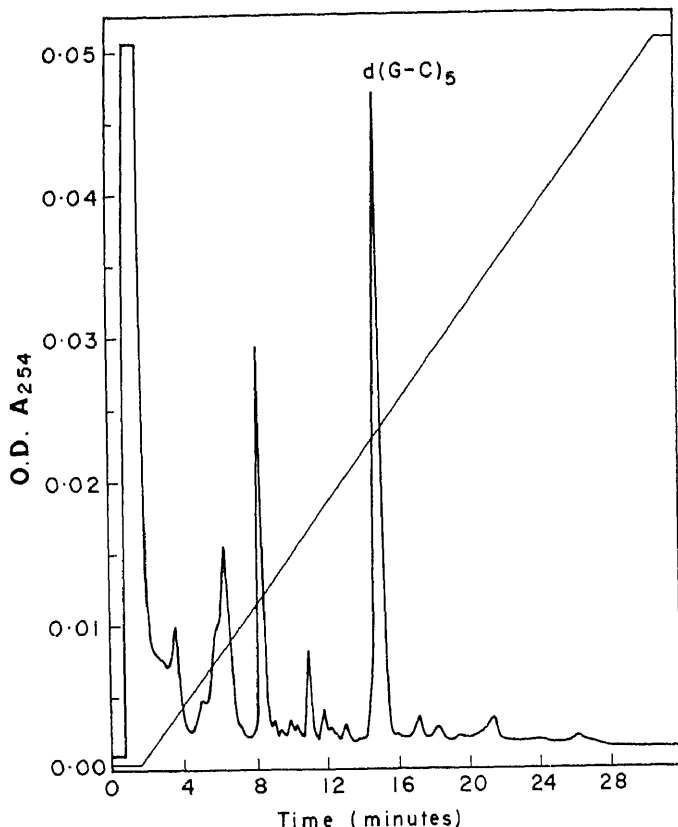


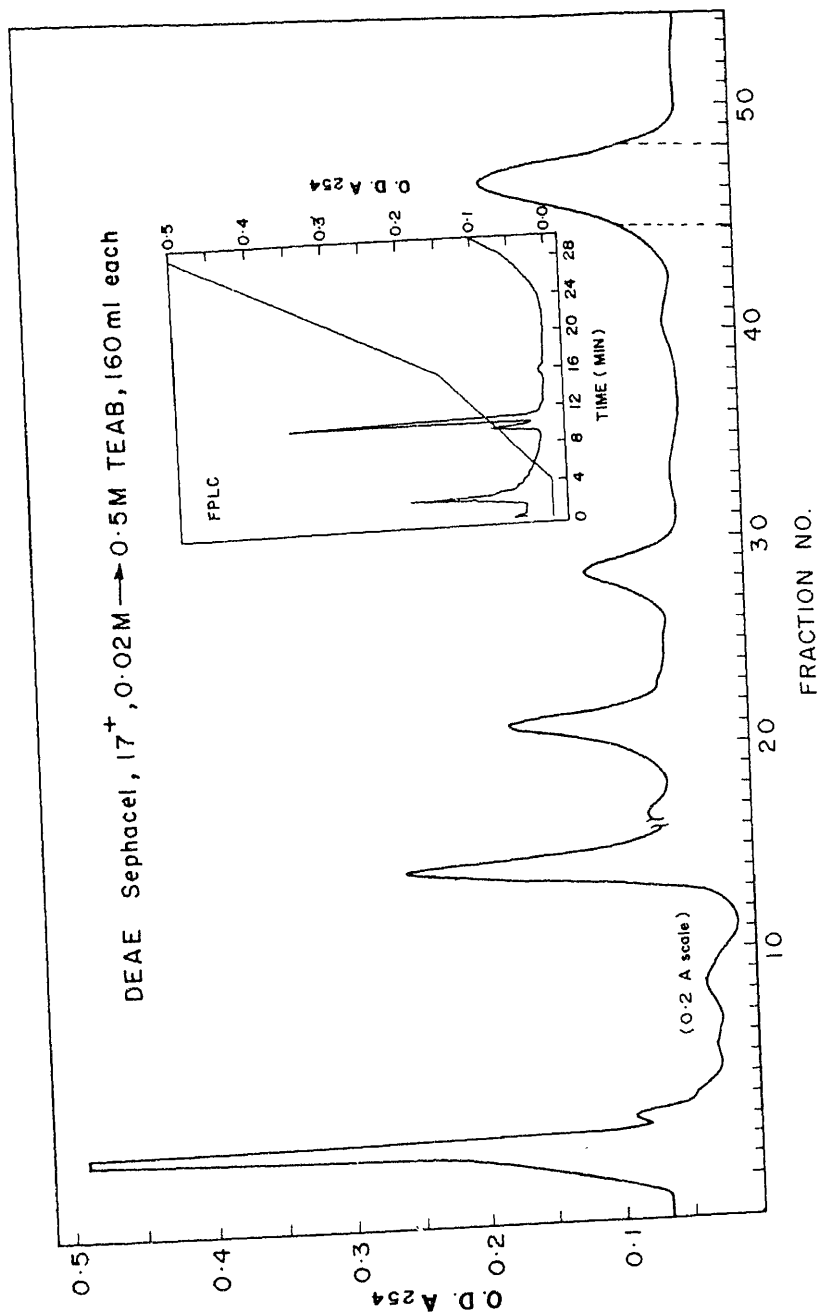
Figure 2. FPLC ion-exchange elution profile of crude product (See § 3 for details).

homogeneity of the product at this stage was demonstrated by a second analytical HPLC run under reverse phase mode on a C18 column.

2.5 The target sequences

The target oligonucleotide sequences required for biophysical studies in our laboratory were $d(G-C)_4$, $d(G-C)_5$ and $d(GGTGGACCTC)$ and these have been prepared by the above procedure. The $d(G-C)_n$ sequences are known to exhibit the left handed Z conformation under certain specific conditions and hence the above sequences of defined lengths are useful in a systematic study of the $B \rightarrow Z$ transitions under a variety of conditions, our particular interest being those transition induced by metal ions. The last decamer sequence is part of a 17 base pair operator region on P22 DNA involved in the interaction with *mnt* repressor. This was required for our studies directed towards understanding the DNA-protein recognition in this system; the *mnt* repressor is being isolated in our laboratory using the cloned plasmids.

We have recently been able to synthesise a 17-mer using a slight modification of our above procedure. Here the condensations were done in pyridine and rest of the cycle



Substances chromatography of 17⁺ (AGGTCCACGGTGGACCT) on DEAE Sephacel. Inset: FPLC analysis of the end peak (enclosed

3. Experimental

The 2'-deoxynucleosides, 4,4'-dimethoxytritylchloride, 2,4,6-triisopropyl benzene-sulphonyl chloride, 4-dimethylamino pyridine and triazole were obtained from Sigma, USA. Trimethylchlorosilane, N-methyl imidazole and dichloroacetic acid (DCA) were procured from Fluka, Switzerland. Pyridine GR (E Merck, India) was refluxed and distilled over ninhydrin followed by distillation over calcium hydride. Acetonitrile and dichloromethane (Extra pure, E Merck India) were distilled over phosphorous pentoxide followed by distillation over calcium hydride. 2,4,6-triisopropyl benzene sulphonyl chloride was recrystallized from hexane (BDH, India), triazole from dioxane and 4-dimethylaminopyridine from diethyl ether. All column chromatographic purifications were done over silica gel H (without binder, BDH, India) by short column method (Still *et al* 1978) and monitored by TLC over silica gel G (BDH, India) coated plates. The spots were visualized by spraying with 60 % perchloric and ethanol (3 : 2) for trityl derivatives (1-8, 15-18). Compounds without trityl group showed black spots on spraying with the above reagent followed by heating.

3.1 6-N-benzoyl,2'-deoxyadenosine (9)

2'-Deoxyadenosine (1.3 g, 5 mmol) dried by coevaporation with pyridine was suspended in 25 ml of dry pyridine and treated with 3.2 ml (25 mmol) of trimethylchlorosilane. The mixture was stirred for 15 min and to this was added 3.0 ml (25 mmol) of benzoyl chloride. The reaction mixture was maintained at room temperature for 2 hrs after which it was cooled in an ice bath and quenched with 10 ml of water. After 5 min it was treated with 10 ml of 29 % aqueous ammonia at room temperature for 30 min, the mixture evaporated to dryness and the residue dissolved in 100 ml of water. It was washed once with diethyl ether and the aqueous layer on cooling yielded 1.5 gm (90 %) of (9).

3.2 4-N-benzoyl-2'-deoxy cytidine (10)

2'-Deoxy cytidine (1.20 g, 5 mmol), in a reaction similar to the above with trimethylchlorosilane (3.2 ml) followed by benzoyl chloride (3.0 ml) in pyridine, (25 ml) yielded 1.5 g (92 %) of (10) on work up.

3.3 2-N-isobutyryl-2'-deoxyguanosine (12)

This was prepared from 2'-deoxyguanosine (0.7 g, 5 mmol), trimethylchlorosilane (3.2 ml) and isobutyrylchloride (4.0 ml) by a procedure similar to that of above. The product (12) crystallised from water was obtained in 70 % yield (1.0 g).

3.4 General procedure for preparation of N-acyl-5'-O-dimethoxytrityl deoxynucleosides

The N-acyl deoxynucleoside (5 mmol) was dissolved in anhydrous pyridine (15 ml) and the solution evaporated to dryness. The solid was dissolved in pyridine (10 ml) and

treated with 4,4'-dimethoxytritylchloride (1.7 g, 6 m mol). The mixture was shaken in the dark for 4 hrs in a sealed flask during which period pyridine hydrochloride separated out. TLC (silica gel) analysis in chloroform:ethanol (90:10 v/v) showed the reaction to be complete as trityl and uv tests showed one positive spot at higher R_f than the starting compound. Methanol (1 ml) was added to the mixture and extracted with chloroform (3 × 40 ml). The organic layer was washed with 1 M aqueous sodium bicarbonate (25 ml) and evaporated to dryness, resulting in a gummy mass. This was chromatographed by the short column method on silica gel H under N_2 atmosphere (1.5 p.s.i.), and eluted with dichloromethane containing 1% triethylamine and increasing amounts of ethanol. The product started eluting around 5% ethanol concentration as monitored by TLC and the appropriate fractions were combined and concentrated. The residue was dissolved in dichloromethane (10 ml) and precipitated by slow addition into a solution of 150 ml of ether:heptane (1:1 v/v) containing 1% triethylamine when the trityl derivatives separated out as amorphous white powder.

3.5 General procedure for preparation of *N*-acyl-5'-O-(4,4'-dimethoxytrityl) 3'-O-(4-chlorophenyl) phosphate triethyl ammonium salts (1-4)

N-acyl-5'-O-dimethoxytrityl-deoxynucleoside (1 m mol) was suspended in anhydrous pyridine (25 ml) and the mixture was evaporated to a final volume of 10 ml. 4-Chlorophenyl phosphorodichloridate (5 m mol) was added to pyridine (10 ml) contained in a glass reaction vessel fitted with a sintered disc and a stopcock and while cooling, water (5 m mol, 90 μ l) was added into the reaction vessel. On leaving the mixture at room temperature for 10 min, pyridine hydrochloride separated out. It was filtered into the reaction flask containing the nucleosides in pyridine under N_2 atmosphere. The mixture was concentrated to 10 ml and after 30 min at room temperature, the phosphorylation was found to be complete as shown by TLC. The reaction was stopped by the addition of 1 M triethyl ammonium bicarbonate (TEAB, 15 ml) at 0°C. It was extracted into chloroform (2 × 75 ml), washed with 0.1 M TEAB and coevaporated to an oil with pyridine. This was then chromatographed over silica gel H by the short column method using 1% triethylamine in dichloromethane and increasing amounts of ethanol. The phosphorylated product eluted as triethyl ammonium salt around 10% ethanol in dichloromethane. The appropriate fractions were pooled and concentrated and the product was precipitated as amorphous white power from dichloromethane solution by adding slowly into ether:hexane (1:1, v/v).

3.6 *N*-acyl-5'-O(4,4'-dimethoxytrityl)-3'-O-succinates (15-18)

The *N*-acyl-5'-O(4,4'-dimethoxytrityl) deoxy nucleosides (9-12, 4 m moles) was dissolved in dry pyridine (25 ml) to which was added succinic anhydride (0.99 g, 9.3 m mol) and stirred with 4-dimethylaminopyridine (1.18 g, 9 m mol). The solution was clear pale yellow within 5 minutes and it was kept stirred at room temperature for 24 hrs at the end of which TLC showed the completion of the reaction. Water (3 ml) was added and the excess pyridine was evaporated under vacuum to yield a gum. This was dissolved in dichloromethane (150 ml), washed twice with aqueous citric acid (810 mg in 100 ml) followed by water, and the dried organic layer concentrated to a gum. The

3.7 Functionalisation of controlled pore glass (CPG)

The long chain alkylamine controlled pore glass (Pierce, 1 g) was dried under vacuum over phosphorous pentoxide and transferred to a 10 ml glass reaction vessel fitted with a G-1 sinter and a stopcock. The filtration is by slight nitrogen pressure on top and the sequence given in table 1 was used for functionalisation of the resin, with volumes of 5 ml per washings. The functionalised resin was dried and a trityl analysis done to get the loading value. The typical values obtained were $A = 32.2 \mu\text{mol g}^{-1}$, $C = 34.7 \mu\text{mol g}^{-1}$, $G = 31.5 \mu\text{mol g}^{-1}$.

3.8 Solid phase assembly and deprotection of the oligonucleotide chains

The assembly was done on an OMNIFIT (Cambridge, UK) manual DNA synthesiser equipped with a 6-way rotary valve and a glass column 5 mm $\times$ 60 mm). The resin (25 mg, 0.9 μm) was transferred into the column and allowed to equilibrate with acetonitrile:dichloromethane (8:2, v/v) after fitting the column end pieces. It was then capped with 20 μl of acetonitrile:acetic anhydride:N-methyl imidazole (8:1:1, v/v) for 10 minutes, followed by cyclical washings indicated below (with a flow rate of 1.5 ml/min driven by dry N_2 gas at 1.5 p.s.i.): (i) acetonitrile:dichloromethane (8:2, v/v) 2 min; (ii) 3% DCA acetonitrile:dichloromethane (8:2, v/v) 6–8 min; (iii) acetonitrile:dichloromethane (8:2, v/v) 2 min; (iv) coupling (stop flow) 15 min.

The coupling mixture in acetonitrile:dichloromethane (8:2, v/v), consisting of the appropriate nucleotide monomer (12 mg, 13 μm), 2,4,6-triisopropyl benzene sulphonyl chloride (20 mg, 65 μm) and 10 μl of N-methyl imidazole, was injected onto the resin with a gas tight syringe through the septum at the top of the column. After the coupling and removal of excess reagents, the trityl washings were collected separately during every cycle for spectrophotometric estimation. This step was omitted after the last coupling to retain the trityl group on the 5'-terminal nucleotide. At the end the resin was thoroughly washed, dried and subjected to deprotection in three stages:

(i) The dry resin in a 2 ml eppendorf tube was treated with *syn*-2-nitrobenzaldehyde

Table 1. Sequence used for functionalisation of the resin.

Treatment	Number of washings	Time per wash (min)	Ninhydrin test
10% diisopropylethyl amine: DMF (v/v)	3	5	
DMF	5	2	Resin +
Nucleoside succinate anhydride ^(a)	1	300	
DMF	5	2	Resin –
Pyridine	5	2	Resin + (trityl test)
Acetic anhydride ^(b) pyridine (1:9, v/v)	1	60	
Pyridine	5	2	Resin –
CH_2Cl_2	5	2	
Ether	5	2	

^(a) Prepared as follows: nucleoside succinate (10 N over the initial resin loading) dissolved in dichloromethane (5 ml) and stirred at room temperature with dicyclohexylcarbodiimide (DCC, 5 N) for 15 min. The mixture is

(35 mg) in 0.5 ml of dioxane: water (1:1, v/v) and 1,1,3,3-tetramethylguanidine (25 μ l) for 20 hr shaking at room temperature. It was filtered, washed a few times with aqueous dioxane (1:1), and the combined filtrate and washings evaporated to an orange gum.

(ii) The gum was treated with 20 ml of concentrated NH_3 (BDH, specific gravity 0.91) in a sealed flask and heated at 60° for 15 hrs. The excess ammonia was evaporated and the aqueous layer was concentrated.

(iii) It was treated with 5 ml of acetic acid:water (80:20, v/v) for 30 min at room temperature and extracted with ether (2 $\times$ 5 ml). The aqueous layer was concentrated, co-evaporated twice with water (3 ml), and redissolved in 2 ml of water.

3.9 General method for purification of oligonucleotide chains

The oligonucleotides were purified using a Pharmacia FPLC system consisting of two P500 pumps, a GP 250 gradient programmer and a 5 MPa mixer. The samples (100 μ l out of 2 ml for analytical runs) were injected through a V-7 (10 MPa) injector and the runs followed spectrophotometrically with Pharmacia (DP-2) dual wavelength monitor fixed at 254 nm. The FPLC column was polyanion S_1 (Pharmacia) and run with phosphate buffer gradient from 0.01 M KH_2PO_4 to 0.75 M KH_2PO_4 in 20% acetonitrile over 30 min with a flow rate of 0.5 ml/min. The product (decamers) eluted under these conditions at about the middle of the gradient (figure 2) and the peak fractions were collected from several runs. The combined fractions were desalted on a water HPLC system using a 160 gel filtration column and eluting with 25% aqueous methanol for 15 min during which a single peak appeared on the chromatogram.

4. Conclusions

In this paper we have demonstrated a convenient protocol for synthesising oligonucleotides by solid phase phosphotriester approach. The detailed methods for synthesis of monomers using indigenous reagents and solvents, functionalisation of the resin, assembly of the chains, deprotection and final purification are described. The paper also demonstrates the utility of the FPLC technique for fast separation of oligonucleotides. Using this procedure, we have synthesised $\text{d}(\text{G-C})_4$, $(\text{G-C})_4$ and $\text{d}(\text{GGTGGACCTC})$ sequences required for biophysical studies in our laboratory.

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Structure of isopropyl-*N*-phenyl carbamate—a plant hormone

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Abstract. The structure of isopropyl-*N*-phenylcarbamate was solved by direct methods and refined to an *R* of 0.123 for 455 observed reflections. The molecule is stabilised by N-H...O hydrogen bonds (2.873 Å). The angle between the phenyl ring and the carbamate group is 31(4)°. Charge density calculations were carried out on this molecule using the Huckel LCAO-MO method for π charges and the DelRe method for σ charges. The charge separation between the ring atom with a net positive charge and the tail methyl group carbons are 5.53 and 5.83 Å.

Keywords. Plant hormone; isopropyl-*N*-phenylcarbamate; carbamate activity.

1. Introduction

The structure of isopropyl-*N*-phenyl carbamate (IPC) was determined as part of a project on plant hormones. IPC is an effective plant growth inhibitor and hence a selective herbicide. It is an isopropyl ester of carbamic acid having antipyretic property, is an inhibitor of photosynthesis and is known to have sedative and hypnotic properties like urethane (an aryl ester of carbamic acid) (Crafts and Robbins 1962). Carbamic acid esters are very active against certain grasses (Templeman *et al* 1945). Usually it is applied to the soil as there should be intimate mixing of the chemical with the soil to bring about injury to the rhizomes (Freed 1951).

Crystal structures of several carbamates, urethane (Bracher and Small 1967), 2-propylpentyl carbamate (DPEC), 4-propylheptyl *N*-phenyl carbamate (DPBC), (Cohen *et al* 1977), ammonium carbamate (Adams and Small 1973), Isomethyl *p*-bromophenyl carbamate (Kartha *et al* 1976), isopropyl-*N* (methyl furoxan) carbamates (INMF) (Calleri *et al* 1977) etc. have been determined in the past. The results from the present study are compared with the earlier one.

2. Experimental

IPC is soluble in *n*-propyl alcohol and on slow evaporation thin needle shaped crystals of the size 0.5 × 0.3 × 0.1 mm are obtained. Its structure and other parameters are: C₁₀H₁₃NO₂; Orthorhombic; *Pca*2₁; *a* = 9.006(6); *b* = 11.788(7); *c* = 9.726(6); *V* = 1042 Å³; *z* = 4; *D_c* = 1.15; *D_m* = 1.13(2) mg m⁻³; *Mr* = 179.2; Melting point = 84°C; λ(CoKα) = 1.7903 Å. As IPC is unstable and sublimes, the crystal was sealed in a lindemann capillary and the space group was uniquely determined to be

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Pca₂₁, from systematic absences. The crystal was mounted on Picker FACS-I four circle diffractometer and the accurate cell parameters were obtained by the least squares fit (Main and Woolfson 1963) for the settings of 21 reflections in the $\pm 2\theta$ values.

The three-dimensional intensity were measured with the Fe filtered CoK α ($\lambda = 1.793$ Å) radiation in the $\theta - 2\theta$ mode for $2\theta \leq 130^\circ$ at a scan rate of 2° min^{-1} . The scan range was 2° and the back grounds were measured for 10 sec each. The intensities were corrected for Lorentz and polarization effects and no absorption correction was applied $\mu(\text{CoK}\alpha) = 1.7082 \text{ cm}^{-1}$, $|F_0| > 2\sigma(F)$ were considered observed.

As the compound was volatile, the quality of data collected were poor and this restricted the accuracy of the results obtained. Nevertheless, due to its importance as a herbicide the conformational analysis was carried out to compare the structure activity of IPC with other plant hormones.

The structure was solved using the program MULTAN (Main *et al* 1980). 163 reflections with $E > 1.2$ were used in phase propagation. The initial R factor for the model came out to be 0.338. After successive block diagonal least squares refinement (Shiono 1968) of the non-hydrogen atoms, with isotropic temperature factors, the reliability index dropped to 0.177. Further cycles of block-diagonal least squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, isotropic temperature factors for hydrogen atoms (from geometry and ΔF synthesis) and Hughes weighting scheme (Hughes 1941)

$$W = 1/F_{\min}^2 \quad \text{for} \quad |F_0| < F_{\min} \quad \text{and} \quad W = 1/|F_0|^2 \quad \text{for} \quad |F_0| \geq F_{\min},$$

where $F_{\min} = 12$ brought down the R -index to 0.127. Two cycles of full matrix least squares refinement using the program LALS (Gantzel *et al* 1961) gave a final R value of 0.123. The hydrogens were assigned isotropic temperature factors of the atoms to which they were bonded and included in the structure factor only and were not refined. Atomic scattering factors for the C, N and O were taken from the International tables (1962) and for the hydrogens from (Stewart 1965).

3. Discussion

The positional parameters are listed in table 1 and the bond length and bond angles are given in table 2. Figure 1 depicts the packing of the molecule down the a -axis. The molecule is in all *trans*-confirmation with C(8)-N(7)-C(5)-O(4) and N(7)-C(5)-O(4)-C(2) torsion angles $-170(3)^\circ$ and $-175(3)^\circ$ respectively. The molecule is stabilized by N-H...O type hydrogen bonds [2.87(4)Å]. The NH...O(6) distance is 2.09 Å and N(7)-H...O(6) angle is $158(3)^\circ$.

The bond distances C(12)-C(13) (1.48(3)) C(1)-C(2) (1.59(5)) and C(2)-C(3) (1.23(5)) deviate from standard values. However only C(2)-C(3) deviation is significant, at 6σ level. This shortening of the bond may be due to the fact that the atom C(3) has a very large thermal vibration. The carbamate group dimensions (table 2) viz., C(5)-N(7) (1.42(6)), C(5)-O(6) (1.19(6)) and C(5)-O(4) (1.32(6)) compare well, within the experimental errors, with the values observed in isomethyl-*p*-bromophenyl carbamate (Kantha 1976), isopropyl-*N* (methyl-furoxan) carbamate (Calleri *et al* 1977) and with other carboxylic acid esters rather than the amides (Bracher and Small 1967).

Table 1a. Positional parameters of non-hydrogen atoms with e.s.d's in parenthesis.

Atom	x	y	z
C1	-0.172 (3)	0.152 (2)	0.397 (3)
C2	-0.038 (4)	0.126 (5)	0.300 (4)
C3	-0.042 (2)	0.032 (2)	0.241 (3)
O4	0.085 (2)	0.171 (2)	0.372 (4)
C5	0.186 (4)	0.218 (5)	0.292 (5)
O6	0.187 (2)	0.232 (2)	0.171 (3)
N7	0.308 (3)	0.250 (2)	0.377 (5)
C8	0.433 (2)	0.320 (2)	0.333 (3)
C9	0.489 (2)	0.310 (2)	0.206 (3)
C10	0.614 (4)	0.368 (5)	0.173 (5)
C11	0.674 (4)	0.451 (6)	0.262 (5)
C12	0.617 (2)	0.463 (2)	0.394 (4)
C13	0.492 (2)	0.389 (2)	0.437 (0)

Table 1b. Thermal parameters with e.s.d's.

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C1	0.023 (3)	0.048 (2)	0.037 (3)	-0.028 (5)	-0.008 (2)	-0.048 (3)
C2	0.032 (7)	0.015 (7)	0.020 (5)	0.001 (4)	0.007 (2)	0.004 (8)
C3	0.040 (8)	0.011 (3)	0.140 (20)	-0.017 (7)	-0.043 (20)	-0.045 (13)
C4	0.012 (3)	0.011 (1)	0.015 (3)	-0.012 (3)	0.000 (6)	-0.007 (4)
C5	0.018 (3)	0.006 (3)	0.017 (3)	0.007 (2)	-0.003 (4)	-0.011 (4)
C6	0.025 (4)	0.022 (6)	0.006 (7)	-0.008 (8)	-0.010 (10)	0.008 (12)
N7	0.025 (1)	0.010 (1)	0.010 (3)	-0.009 (3)	-0.005 (2)	0.001 (1)
C8	0.014 (2)	0.013 (1)	0.014 (2)	-0.009 (2)	0.000 (3)	0.013 (3)
C9	0.021 (2)	0.011 (1)	0.012 (3)	-0.008 (2)	0.002 (1)	-0.004 (2)
C10	0.023 (3)	0.011 (5)	0.021 (2)	-0.009 (2)	-0.009 (1)	0.001 (4)
C11	0.014 (4)	0.016 (7)	0.026 (5)	-0.012 (1)	0.006 (1)	-0.002 (3)
C12	0.016 (2)	0.018 (2)	0.018 (3)	-0.001 (3)	-0.004 (2)	0.006 (3)
C13	0.014 (3)	0.011 (2)	0.021 (3)	-0.011 (4)	-0.002 (5)	-0.001 (4)

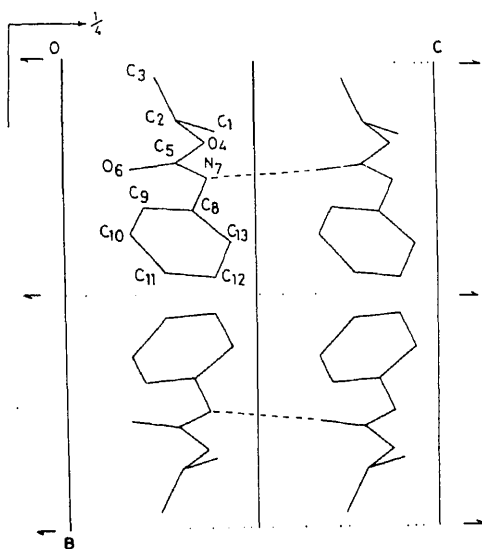
the temperature factor is of the form: $t = \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$.

planes is 31(4)°. This angle is 21° and 9° in the two independent molecules of isopropyl-N (methyl furoxan) (Calleri *et al* 1977).

It has been observed that in auxins, another class of plant hormones, where the carboxyl group is at the tail end of the molecule the angle between the rigid ring group and the carboxyl group is found to be 90° in active auxins and 0° in inactive auxins (Raghunathan and Vasantha Pattabhi 1981). ipc differs from auxins in having two methyl groups at the tail instead of a carboxyl group. The angle between the tail group viz. the plane through atoms C(1), C(2) and C(3) and the phenyl group is 32(4)°. However, the carbamate group makes 117(4)° with the plane through the tail group. In table 4, τ_2 refers to the angle between the rigid nucleus, like aromatic group and the

Table 2. Bond lengths (Å) and bond angles (°) with e.s.d's in parentheses.

C1—C2	1.59 (5)	C1—C2—C3	115 (3)
C2—C3	1.23 (5)	C1—C2—O4	101 (2)
C2—O4	1.43 (5)	C3—C2—O4	125 (3)
O4—C5	1.32 (6)	C2—O4—C5	113 (3)
C5—O6	1.19 (6)	O4—C5—O6	130 (3)
C5—N7	1.42 (6)	O4—C5—N7	107 (3)
N7—C8	1.46 (3)	O6—C5—N7	122 (3)
C8—C9	1.34 (4)	C5—N7—C8	125 (3)
C9—C10	1.36 (5)	N7—C8—C9	121 (2)
C10—C11	1.41 (8)	N7—C8—C13	114 (2)
C11—C12	1.40 (6)	C9—C8—C13	121 (2)
C12—C13	1.48 (3)	C8—C9—C10	119 (2)
C13—C8	1.40 (3)	C9—C10—C11	121(4)
		C10—C11—C12	120 (3)
		C11—C12—C13	119 (2)
		C12—C13—C8	115 (1)

**Figure 1.** Packing of the molecule down the *a* axis.**Table 3.** Distance of separation between the oppositely charged atoms in IPC. The average σ is about 0.04 Å.

N7 C1	4.47
N7 C3	4.27
C8 O4	3.61
C8 O6	2.91

Table 4. Conformational parameters in some carbamates

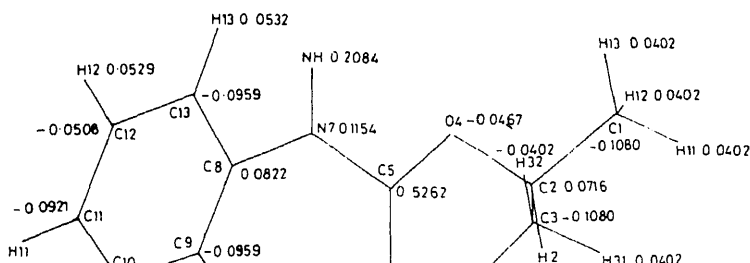
Name	NCOC(°)	CNCO(°)	τ_1 (°)	τ_2 (°)	References
Polyurethane	176.9 (7)	179.3 (6)	13.77	84.69	1
Ethyl carbamate	-179.24 (60)	0.96 (4)	1.50	—	2
DPBC	179.10 (36)	2.00 (68)	53.13	72.51	3
DPEC	179.81 (29)	—	—	59.9	3
INMF				70.3	
Isomer A	-179.53 (13)	92.50 (64)	159.13	88.77	4
Isomer B	171.15 (20)	3.93 (38)	54.70	50.30	4
IPC	-175 (3)	-170 (3)	31 (4) ^o	32.4	Present work

τ_1 Angle between the rigid nucleus like aromatic group and the carbamate group plane; τ_2 angle between the rigid nucleus and the tail group plane. 1. Foreier *et al* (1981); 2. Bracher *et al* (1967); 3. Cohen *et al* (1977); Calleri *et al* (1977).

has a preference for gauche conformation. The N-C-O-C (NCOC) group prefers *trans*-configuration in all the structures compared in table 4.

In order to compare the results obtained in this study with another class of plant hormones, viz., auxins, we have performed charge density calculations on the IPC molecule. The σ charges were calculated by the DelRe method (DelRe 1958) and the π charges using Huckel LCAO-MO method (Pullman and Pullman 1963). The net fractional charges on each atom is shown in figure 2. The distance of separation between the oppositely charged atoms of the ring group and the side chain are listed in table 3.

According to the charge separation theory on auxins (Porter and Thimann 1965) the critical distance of separation between the net positive charge present in the rigid nucleus and the carboxyl group oxygen is about 5.5 Å, for them to be active. An attempt has been made to see whether this theory can be applied to IPC, a different class of hormone, viz., carbamate. In IPC the distance of separation between the negatively charged methyl carbons and the positively charged C(8) atom of the ring are viz., C(8) . . . C(3) 5.53(5) and C(8) . . . C(1) 5.82(5) Å which can be compared.



Acknowledgement

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Influence of imidazole and bifunctional nucleophiles on the micellar catalysed hydrolysis and hydroxylaminolysis of esters

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Abstract. Though 2- and 3-hydroxypyridines, structurally resemble imidazole, 2-hydroxypyridine seems to function as a nucleophile in the hydrolysis of *p*-nitrophenylbenzoate as it can acquire a pyridine form (Mosher 1959) while the latter cannot. The bifunctional activity of benzamidine has also been enhanced by anionic micelles of sodium laurylsulphate. The anionic micelle formed by sodium laurylsulphate retards the rate of hydroxylaminolysis of *p*-nitrophenylbenzoate, while the cationic micelle formed from cetyltrimethylammonium bromide enhances the rate in $\text{H}_2\text{NOH}\cdot\text{H}_2\text{NOH}\cdot\text{HCl}$ buffer at $\text{pH} = 6.14$. Such behaviour is in favour of the anion, H_2NO^- , acting as a nucleophile to some extent. On the contrary, hydroxylaminolysis of *p*-nitrophenylphenylmethane sulphonate (PMS) proceeds at a slower rate and imidazole catalysis is observed as these esters at $\text{pH} = 6.14$ possibly prefer a $B_{\text{Ac}} 2$ mechanism, which is absent at $\text{pH} = 9.2$ as the same reactions proceed by a E_{1cB} path.

Keywords. Catalysis; imidazole; 3-hydroxypyridine; 2-hydroxypyridine; benzamidine; hydrolysis; hydroxylaminolysis.

1. Introduction

As bifunctional nucleophiles can concertedly attack the carbonyl carbon of an ester and deliver a proton to the carbonyl oxygen, an intermediate will be formed without the creation of charge. In this communication we report the effect of benzamidine, 2-hydroxypyridine and 3-hydroxypyridine on the hydrolysis of *p*-nitrophenylbenzoate (PNPB) in micellar media.

Also, hydroxylamine can function as an ambient nucleophile, which can attack at the carbonyl carbon of an ester either from the oxygen or the nitrogen end, yielding acetohydroxymic acid as a final product, as proposed in the case of a thiol ester (Bruce and Fedor 1964) as well as in the reaction of amides and hydroxylamine (Alburn and Grant 1965). This communication also includes a study of the micellar influence on the hydroxylaminolysis of carboxylic, sulphate and phosphate esters, which is used to decide the mode of attack by NH_2OH . The imidazole catalysis of the hydroxylaminolysis of these esters at this $\text{pH} = 6.15$ points to the operation of a different mechanism.

2. Results and discussion

2.1 Catalysis by 2- and 3-hydroxypyridines

The catalysis of the hydrolysis of several esters by added imidazole (Bender and Turnquest 1957; Bruce and Schmir 1957; Jencks 1969) and by a number of micelles

bearing an imidazolyl group (Brown and Bunton 1974; Moss *et al* 1975; Tagaki *et al* 1979) have been documented in literature. Though imidazole catalyses many hydrolytic reactions, it lacks the bifunctional activity exhibited by related compounds. The present work is on the effect of 2- and 3-hydroxypyridines, which are structurally similar to imidazole, on the hydrolysis of PNPB. 2-Hydroxypyridine is known to function as a bifunctional catalyst (Swain and Brown 1952).

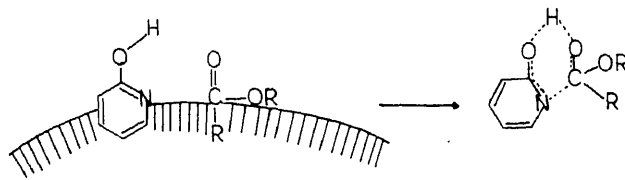
In the present study both 2- and 3-hydroxypyridines alter the rate of hydrolysis of PNPB only in the presence of micelles (table 1). The rate enhancement observed in the rate of hydrolysis of PNPB due to added 2-hydroxypyridine both in cationic and anionic micellar phase may be due to 2-hydroxypyridine (2-HP) acquiring a pyridone form (Mosher 1959) and hence possessing a reduced phenolic character. But the added 3-hydroxypyridine (3-HP) accelerates the rate in the presence of sodium lauryl sulphate (SLS) and retards the rate in the presence of cetyl trimethylammonium bromide (CTAB) possibly due to its inability to acquire the pyridone form. As the catalysis by 2-HP is observed only in the micellar phase, the results possibly suggest that the proximity and proper orientation of 2-HP in the micellar phase assist the bifunctional nature of this compound (figure 1) as ketones are most likely to be solubilised near the surface or in the head group region with the carbonyl oxygen pointing towards the surface (Balasubramanian *et al* 1982).

Table 1. Influence of hydroxypyridines on the rate of hydrolysis of PNPB in the presence and absence of micelles^a.

[Hydroxypyridine]* M	3-HP			2-HP		
	b	c	d	b	c	d
	$10^4 k_{\text{obs}} \text{ s}^{-1}$			$10^4 k_{\text{obs}} \text{ s}^{-1}$		
0.00	5.5	0.61	12.3	5.5	0.61	12.3
0.25	5.6	0.73	11.2	4.8	0.72	12.4
0.50	5.6	0.85	10.2	4.6	0.72	13.8
1.00	5.3	1.03	9.3	4.8	0.78	14.5
1.50	5.5	1.98	9.1	5.3	0.99	—
2.0	5.3	2.0	9.0	5.3	1.16	16.5

* The values in this column refer to 10^2 [3-HP] or 10 [2-HP];

^a reactions were carried out at 30°C at pH = 9.2 and [PNPB] = 1.50×10^{-5} M at $\mu = 0.10 \text{ mol dm}^{-3}$; ^b in the absence of micelles; ^c in 0.010 M SLS; ^d in 0.0010 M CTAB.



The observed catalysis by 2-HP may also be partly due to a smaller change in pK_a value in micellar media wherein the presence of the anionic form may increase the nucleophilicity of 2-HP (pK_a value for 2-HP is 10.6 at 30°C and it is 10.0 in 0.0010 M CTAB and 9.4 in SLS; pK_a value for 3-HP is 4.3 at 30°C and 4.2 in 0.0010 M CTAB and 4.4 in 0.010 M SLS).

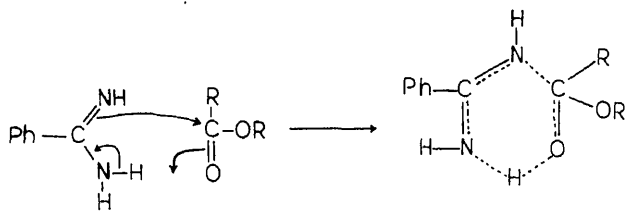
2.2 Catalysis by benzamidine

Menger (1966) observed 15 000 fold rate enhancement in the reaction of benzamidine with PNPB in chlorobenzene at 25°C, which has been attributed to its bifunctional nature. In the present study also the benzamidine added catalyses the hydrolysis of PNPB both in the presence and absence of micelles (table 2). Benzamidine, because of its bifunctionality, may favour the formation of a tetrahedral-like intermediate through a six-membered transition state (figure 2). The catalytic efficiency of benzamidine is enhanced in an anionic micellar phase compared to the cationic micellar phase probably due to partial reduction in the nucleophilicity of benzamidine on the cationic surface. Nevertheless, the catalysis by benzamidine observed in presence of both anionic and

Table 2. Effect of added benzamidine on the rate of hydrolysis of PNPB in the presence and absence of micelles*.

[Benzamidine]	$10^4 k_{\text{obs}} \text{ s}^{-1}$				
	PNPB			PDI ^d	PMS ^e
	a	b	c		
0.00	5.5	0.61	12.3	2.3	21
0.0040	—	1.58	16.0	—	—
0.0086	—	2.5	—	—	—
0.016	6.4	3.4	18.4	—	—
0.050	8.4	5.0	31.	—	23
0.10	13.2	—	38	—	25
0.20	29	—	62	0.78	20
0.38	—	—	—	0.77	—

* Reactions were carried out at 30°C at pH = 9.2 and $\mu = 0.10 \text{ mol dm}^{-3}$ and $[\text{PNAB}] = 1.50 \times 10^{-5} \text{ M}$; ^a in the absence of micelles; ^b in 0.010 M SLS; ^c in 0.0010 M CTAB; ^d for PDI in 0.0010 M CTAB; ^e for PMS in 0.0010 M CTAB.



cationic micelles seem to be very much like that of 2-HP. Also such catalysis has not been observed in the case of PMS and PDI which prefer the E_1cB path at pH = 9.2 (table 2).

2.3 Hydroxylaminolysis of esters and imidazole catalysis

The rate of hydroxylaminolysis of PNPB depends on the first power of concentration of the ester both in the presence and absence of SLS or CTAB. In the concentration range of 0.010 M to 0.50 M, the reaction exhibits a first order dependence on hydroxylamine concentration. Hence the rate-law for the reaction can be given as

$$\text{rate} = k[\text{ester}][\text{H}_2\text{NOH}]. \quad (1)$$

Cationic detergents CTAB, CDBAC (cetyldibenzylammonium chloride) or CPC (cetylpyridinium chloride) added increase the rate marginally at lower concentrations of detergent but retard the rate at higher concentrations (table 3). The catalytic effects of cationic surfactants on the reaction seems to be less significant, probably because the reactions have been carried out at acidic pH = 6.14 where there is only a slight difference in the structures of the transition state and the initial ester (Geneste *et al* 1976).

There is considerable retardation in rate with an increasing concentration of SLS (table 4), which is generally observed for reactions involving a nucleophilic attack on the carbonyl carbon of esters. Coupled with the rate enhancement observed in the

Table 3. Effect of added cationic detergent on the rate of hydroxylaminolysis of PNPB.

$10^4 [\text{Detergent}] \text{ M}$	$10^3 k_{\text{obs}}^* \text{ s}^{-1}$		
	CTAB	CDBAC	CPC
—	1.12	1.12	1.12
0.050	—	—	2.3
0.50	1.61	2.1	2.4
1.000	1.70	2.3	2.8
5.0	0.76	1.90	1.87

* At 30°C, pH = 6.15, [buffer] = 0.10 M, in 2.5% CH_3CN and 97.5% H_2O (v/v) and $[\text{PNPB}] = 3.0 \times 10^{-5} \text{ M}$.

Table 4. Influence of SLS on the rate of hydroxylaminolysis of PNPB.

$10^2 [\text{SLS}] \text{ M}$	$10^3 k_{\text{obs}}^* \text{ s}^{-1}$
—	6.0
0.25	4.0
0.50	2.2
1.00	1.58
2.5	0.90
5.0	0.68
10.0	0.60

* At pH = 6.15, [buffer] = 0.10 M, 30°C, in 2.5% CH_3CN and 97.5% H_2O

cationic micelle in the hydroxylaminolysis of esters, the above rate-retarding effect of SLS suggests an attack on the carbonyl carbon of esters by the oxygen end of H_2NO^- at this pH.

Using Menger and Portnoy's treatment (1967), the substrate-micelle binding constant (K_s/N) has been evaluated from this data to be $2.9 \times 10^2 \text{ M}^{-1}$ (where N is the aggregation number). The cooperativity index, n , calculated using the Piskiewicz's equation (1977) is 1.4, indicating a positive interaction between the anionic micelle and the substrate.

The rate of hydroxylaminolysis of PMS(I) and PDI(II) is slow at pH = 6.15 and the specific rate of hydrolysis of these esters at pH = 9.2 is least affected by added imidazole. As the hydrolysis of PMS and PDI preferably follows the E_1cB path at this pH, imidazole has no effect on these reactions. As the sulphur and phosphorus centres involved in the E_1cB path seem to deter the nucleophilic attack by imidazole, similar reactivity is expected for the nitrogen end of H_2NOH . But the formation of a such an anion (A) is not favoured at pH = 6.15 and the E_1cB path will be less favoured at this pH. As the added imidazole does catalyse the hydroxylaminolysis of sulphate and phosphate esters at pH = 6.15, these esters probably prefer the $B_{Ac}2$ path at this pH. From the above results on the hydroxylaminolysis of esters, coupled with imidazole catalysis, E_1cB or $B_{Ac}2$ mechanisms have been assigned to the reactions.

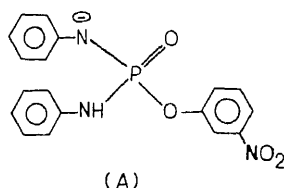
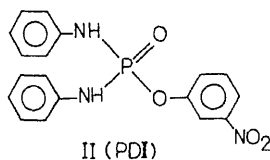
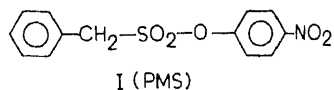


Chart 1.

3. Experimental

3.1 Materials

PNPB was prepared following the procedure in Vogel (1978). *p*-Nitrophenylphenylmethane sulphonate (PMS) was prepared by the procedure of Davy *et al* (1977). The ester, *m*-nitrophenyl-N,N-diphenylphosphorodiamidate was prepared by refluxing a mixture of aniline, POCl_3 and *m*-nitrophenol in the ratio 2:1:1 in the presence of catalytic amounts of pyridine. The refluxing was continued for 4 hrs and then the mixture was cooled and the solid compound which separated, recrystallised from chloroform-hexane mixture. The purity of the compound was checked by the TLC technique (m.p. 172°C).

The surfactants were of extra pure variety (BDH/Aldrich) and were further purified by

All the hydrolytic reactions were carried out at pH = 9.2, maintaining the pH with borax buffers while the kinetics of hydroxylaminolysis of PNPB was studied at $k = 6.15 \times 10^{-4} \text{ s}^{-1}$ in 2.5% CH_3CN -97.5% H_2O (v/v) at 30°C at an ionic strength maintained by using 0.50 M NaCl. A solution of the required pH was prepared by titrating a solution of the buffer agent of known concentration against a standard acid (carbonate free), pH being measured with a digital pH meter (of 0.010 accuracy). Whenever surfactants were employed the pH of the buffer solution was adjusted to maintain the presence of the required concentration of surfactant.

3.2 Rate measurements

The reactions were studied by monitoring the increase in absorbance due to the formation of the *p*-nitrophenoxide ion at 400 nm or *p*-nitrophenol at 320 nm on a Cary 14 spectrophotometer provided with a thermostatic cell compartment. The hydrolytic reactions were conducted at 30°C and at 0.10 ionic strength, maintained by using 0.10 M NaCl, unless otherwise mentioned. The reactions were studied for four half-lives and the rate constants were evaluated from the slopes of the regression lines for correlation of $\log(A - A_\infty)$ versus time. The linear regression analysis was performed on a micro 2200 programmable calculator (Hindustan Computers, New Delhi).

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Syntheses of some N-substituted hydrazines by the anhydrous chloramine process

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Abstract. Chloramine, produced in the gas phase by the reaction of chlorine and ammonia, reacts with various primary and secondary amines in nonaqueous solvents in the presence of a fixed base to form the corresponding N-substituted hydrazines. The hydrazines synthesised include phenylhydrazine, *p*-tolylhydrazine, β -aminoethylhydrazine, N-aminopyrrolidine and N-aminopiperidine. Apparently, no hydrazine is formed when the reaction is carried out in the absence of fixed base. The effect of various factors, such as fixed base concentration, amine/chloramine ratio etc., on the overall yield of hydrazines has been studied. In this context, a modified chloramine gas generator giving improved yields is described. The optimum yield of chloramine is shown to be dependent upon the ratio of chlorine, ammonia and nitrogen taken, but is virtually independent of the reactor temperature.

Keywords. Synthesis; substituted hydrazines; chloramine process.

1. Introduction

Extensive use of hydrazines as storable liquid rocket fuels has led to renewal of interest in their synthesis. In most instances, the synthetic methods available are cumbersome, requiring multiple step separations from dilute aqueous solutions and, therefore, are expensive. Realising this, Jain *et al* (1980) recently adopted an alternate procedure wherein the synthesis of monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) (Sisler *et al* 1981) could be carried out in nonaqueous solvents instead, using the anhydrous chloramine process (Sisler *et al* 1954).

Studies leading to the synthesis of aryl and other substituted hydrazines by the chloramination process are indeed scanty. Sisler and coworkers (Sisler *et al* 1961; Omietanski *et al* 1956) reported the synthesis of phenylhydrazine and N-aminopiperidine by reacting gaseous chloramine with aniline and piperidine, respectively, taken in large excess. In contrast to these studies, ethereal solutions of chloramine have been reported (Jaffari and Nunn 1971) to react with anilines resulting in the formation of oxidation products, the azobenzenes. In view of the results of our recent studies on the synthesis of MMH and UDMH, however, it is interesting to find out if the aryl hydrazines could be synthesised in a similar way i.e. in nonaqueous solvents in the presence of a fixed base. In the present study we have examined the reactions of gaseous chloramine with anilines and some other amines of interest, the results of which are reported.

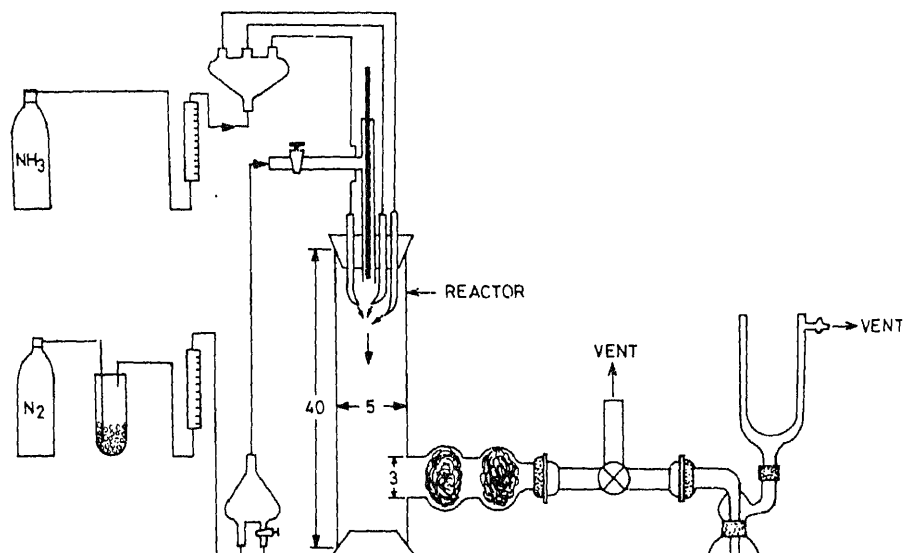
2. Experimental

2.1 Chloramine gas generator

In Sisler's process, chloramine gas is produced by the gas phase reaction of chlorine and ammonia (Sisler *et al* 1954).



The main difficulty encountered in this production is the choking of the chlorine inlet to the chloramine generator by the ammonium chloride formed. To minimise this difficulty and to get better yields of chloramine the chloramine generator described in the literature (Sisler *et al* 1954) has been suitably modified. A schematic diagram of the modified generator is presented in figure 1. It consists of a vertical reactor wherein gaseous chlorine and ammonia are allowed to react. The amounts of the gases passing through the reactor were metered using previously calibrated flow meters (rotameters). The reactor is a cylindrical glass tube 40 cm long and of 5.0 cm dia, having a side tube near the bottom. This side tube (3 cm dia) contains two bulbs of dia 5 cm each which are loosely packed with glasswool to trap the ammonium chloride produced in the reaction. Both the ends of the main tube of the reactor are fitted with rubber stoppers. At the top end, the stopper is fitted with 4 glass tubes; one a 10 mm glass tube at the centre and the other three being 8 mm glass tubes symmetrically arranged around it. Ammonia is introduced through these three tubes whose ends are formed into jets



pointing towards the centre. The mixture, chlorine plus nitrogen, is introduced through the central tube. A glass rod inserted in this tube helps in periodically removing choking, if any.

To generate chloramine in solution, about 500 ml ether is taken in the reaction vessel connected to the chloramine generator through a three-way stopcock as shown in figure 1. The outlet of this vessel is attached to a vent through a cold finger. The reaction is set to the required temperature by means of a heating tape. The system is first flushed by passing nitrogen and then specified amounts of ammonia and chlorine are introduced into the system. The production of ammonium chloride becomes immediately evident as it fogs the generator. The effluents of the chloramine generator are bubbled through a known volume of ether for a specified time, wherein the chloramine formed is dissolved in it. After completing the run, the ether solution is kept open to the atmosphere for 2 hrs for the volatile gases to escape. Chloramine present in the ether solvent is then estimated by the iodometric method and the % yield calculated by the method given by Sisler *et al* (1954).

A series of experiments were conducted to explore the effect of various factors on the yield of chloramine. These include (i) the temperature of the reactor wall (ii) the introduction of excess ammonia over the stoichiometric equivalent of chlorine, (iii) the introduction of excess nitrogen as carrier gas and (iv) the time of the experimental run. Some of the typical results of this study are given in table 1.

2.2 Materials and analysis

All of the solvents and amines were of reagent grade. The liquid amines were freshly distilled before use.

The hydrazine content of the reaction mixture was estimated by the iodate method. The applicability of this method to aromatic hydrazines was ascertained by actually estimating the hydrazine content in a known amount of freshly distilled phenylhydrazine.

Table 1. Chloramine yield data.

Flow rate ratio (mmol hr ⁻¹) Cl ₂ :N ₂ :NH ₃	Mole ratio Cl ₂ :N ₂ :NH ₃	Time (min)	Temperature (°C)	Rate of chloramine formation (mmol hr ⁻¹)
164:1590:1680	1:9.7:10.2	17	25	69.2
164:1600:1680	1:9.8:10.2	17	95	71.1
164:1600:1650	1:9.8:10.1	60	58	54.1
164:1590:640	1:9.7:3.9	15	26	36.2
164:1600:1130	1:9.8:6.9	15	27	53.3
164:1590:2050	1:9.7:12.5	15	26	54.2
124:820:1270	1:6.6:10.2	15	26	19.0
124:1280:1270	1:10.3:10.2	15	27	38.9
124:1680:1270	1:13.5:10.2	15	27	46.1
134:870:1020	1:6.5:7.6	60	58	41.3
124:1280:1650	1:9.7:11.6	60	58	50.4

exchange spectra. The IR spectra were recorded with a Perkin-Elmer-781 spectrophotometer as nujol mulls.

2.3 Reaction of the chloramine-ammonia mixture with aniline

In a typical reaction, a cylindrical reaction vessel of 650 ml capacity was charged with a 350 ml methanol solution containing 252 mmol of KOH and 378 mmol of freshly distilled aniline. The inlet of this vessel was attached to the chloramine generator, and the outlet to a vent via a cold finger. Approximately 63 mmol of chloramine was bubbled through the methanol solution over a period of one hr. A white solid material precipitated and the solution turned brown. The solution was kept undisturbed for 2 hrs to allow the volatile gases to escape. The solid material was then filtered off and found to be potassium chloride by the flame test and chloride analysis. The filtrate was estimated for its hydrazine (total N-N bonded material) content by the iodate method. It was found to contain 44 mmol, or 70% yield of phenylhydrazine based on chloramine.

The presence of phenylhydrazine in the reaction mixture was confirmed by preparing its benzaldehyde derivative. For this, a known volume of the chloraminated solution was carefully neutralized by concentrated hydrochloric acid till it became slightly acidic. To this solution, an equivalent amount of benzaldehyde dissolved in minimum amount of methanol, was added. A yellow precipitate was formed immediately, which was filtered, recrystallised from dilute ethanol and dried under vacuum. The derivative was characterized by its melting point, elemental analysis, IR and NMR spectra (table 2). The spectral features were identical to those obtained using an authenticated sample of benzaldehydephenylhydrazone. The yield data of phenylhydrazine obtained using different mole ratios of chloramine:amine:KOH are given in table 3.

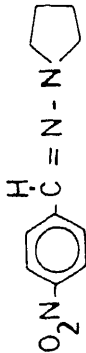
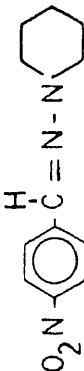
The chloramination procedure used for other amines was the same as that used in the case of aniline. The salient features of each reaction are described below. The analytical data of the derivatives are given in table 2.

When a mixture of 13.5 g (126 mmol) of *p*-toluidine, 7.1 g (127 mmol) of KOH in 350 ml methanol was chloraminated for 45 min (47 mmol of chloramine), the amount of the N-N bonded product formed was found to be 20.3 mmol corresponding to a yield of 43% *p*-tolylhydrazine, based on chloramine. The benzaldehyde derivative was prepared by refluxing the neutralized reaction mixture (using HCl) and benzaldehyde for 2½ hrs, and subsequently cooling it in ice and salt mixture.

When a methanolic solution (300 ml) containing 10.5 ml (126 mmol) of pyrrolidine and 7.0 g (125 mmol) of KOH was chloraminated for one hour (63 mmol, chloramine), 53 mmol of N-N bonded material was obtained corresponding to a yield of 85% N-aminopyrrolidine. The formation of N-aminopyrrolidine was confirmed by preparing and characterizing its *p*-nitrobenzaldehyde derivative; by neutralizing the chloraminated mixture by glacial acetic acid and reacting it with *p*-nitrobenzaldehyde.

The chloramination of piperidine was carried out using various ratios of amine:KOH:chloramine. The yield data are given in table 4. The formation of N-aminopiperidine was confirmed by its *p*-nitrobenzaldehyde derivative, which was

Table 2. Characterization of hydrazine derivatives^a.

Compound	Elemental analysis						¹ H NMR chemical shifts (δ)	IR absorptions (cm ⁻¹)	
	m.p. °C	Found %		Calculated %		°N-N		°C≡N	
		C	H	C	H				
N-(4-nitrophenylmethylene)-1-pyrrolidinamine 	102	60.27	6.28	60.26	5.98	7.5, 8.1 (4H, Ar); 7.03 (H, CH); 2.4 (4H, CH2); 3.43 (4H, NCH2)	1100	1590	
N-(4-nitrophenylmethylene)-1-piperidinamine 	65	62.04	6.59	61.79	6.48	7.7, 8.1 (4H, Ar); 7.5 (H, CH); 1.66 (6H, CH2); 3.27 (4H, NCH2)	1100	1600	

^a The observed and reported (in parentheses) melting points of the benzaldehyde derivatives of phenylhydrazine and *p*-tolylhydrazine respectively, are 154 (158-159) and 115 (114)°C (Reut and Pawlowski 1903). The elemental analysis, IR and ¹H NMR data of these compounds are in agreement with the assigned structures. The m.p. of the dioxalate derivative of β-aminoethylhydrazine is 204 (206)°C (Gever and Hayes 1949). It was characterized by its elemental analysis and IR spectrum.

Table 3. Reaction between chloramine^a and aniline in methanol in the presence of KOH.

Mole ratio CA: amine: base (mmol)	Ratio CA: amine: base	Amount of phenylhydrazine formed (mmol)	Yield based on CA (%)
63:63:0	1:1:0	0	0
63:63:63	1:1:1	0	0
63:63:252	1:1:4	13.6	22
63:126:252	1:2:4	28.5	45
63:252:252	1:4:4	38.6	61
63:378:252	1:6:4	44.3	70
63:378:126	1:6:2	38.2	61

^a Chloramine = CA.**Table 4.** Reaction between chloramine^a and piperidine in methanol in the presence of KOH.

Mole ratio CA: amine: base (mmol)	Ratio CA: amine: base	Amount of N-aminopiperidine formed (mmol)	Yield based on CA (%)
63:63:0	1:1:0	0	0
63:63:63	1:1:1	0	0
63:63:126	1:1:2	25.4	40
63:126:127	1:2:2	31.4	50
63:189:126	1:3:2	27.3	43
63:63:189	1:1:3	30.4	50

^a Chloramine = CA.

obtained by refluxing the neutralized mixture and *p*-nitrobenzaldehyde for 2½ hrs.

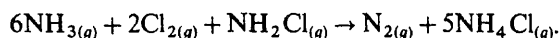
When a mixture of ethylenediamine (250 mmol) and KOH (250 mmol) in 300 ml methanol was chloraminated for one hour (63 mmol chloramine), the conversion to β -aminoethylhydrazine was found to be 51 %. The formation of β -aminoethylhydrazine was confirmed by preparing its dioxalate derivative, by the method reported by Gever and Hayes (1949).

In all of the above cases, when the chloramination was carried out in the absence of KOH, there was no evidence of the presence of any N–N bonded compound in the reaction products.

3. Results and discussion

It is obvious that chloramine gas could be generated in fair yields using the modified generator. In order to optimise the chloramine yield, a series of experiments were carried out, the results of which are summarized in table 1. It is observed that the

portion with the excess of ammonia up to a certain ammonia to chlorine mole ratio. However, it is interesting to note that a significant increase in the yield is also observed with the introduction of excess nitrogen which is known to act only as a carrier gas. Hence, the introduction of excess ammonia or nitrogen improves the rate of total gas flow away from the primary reaction zone, these results suggest that the increased flow rate may prevent or suppress the decomposition of chloramine by the reaction (Sisler *et al* 1954):



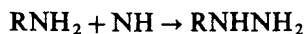
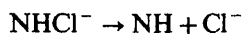
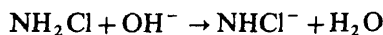
The above reaction could occur at the lower flow rates by bringing the chloramine gas back into the primary reaction zone and thereby getting it oxidized to nitrogen. It may also be noticed that this oxidation causes a sharp decrease in the total gas flow rate, which again will result in the reduction of the total gas flow, and this in turn further enhances the decomposition of chloramine.

The temperature of the reactor wall does not seem to have any effect on the chloramine yield in the range 25 to 95°C, although Sisler *et al* (1954), observed considerable decomposition of chloramine when the reactor walls are kept below the ambient temperature i.e. in the range 10 to -30°C.

There is, however, a decrease in percentage chloramine yield with the time of the run. As the reaction proceeds, the glasswool placed in the side tube continuously traps the ammonium chloride formed in the reaction. Consequently, the retention time of chloramine near the reaction zone increases with the time. Because of this, the decomposition of chloramine by the reaction (mentioned above) occurs to some extent, resulting in the low percentage yield of chloramine.

From the results of the chloramination reactions, it is evident that chloramine reacts readily with various amines in non-aqueous solvents in the presence of a fixed base such as KOH, resulting in the formation of the corresponding hydrazines in good yields. The experimental data of phenylhydrazine and N-aminopiperidine, given in tables 3 and 4, show that hydrazines could be synthesised using amine to chloramine ratios as low as 1:1 at appropriate fixed base concentrations. This is in striking contrast to the twenty to thirty-fold excess of aniline or piperidine needed to obtain the corresponding hydrazines in satisfactory yields using the earlier methods (Omietanski *et al* 1956; Sisler *et al* 1961) involving chloramination of these amines taken as neat liquids.

The present study also reveals the importance of the fixed base in the synthesis of hydrazines in nonaqueous solvents. Apparently no hydrazine is formed when the reaction is carried out in the absence of KOH. These results are parallel to those obtained recently by Jain *et al* (1980) and earlier by Audrieth and Diamond (1954b) and Berg and Schmidt (1951). These data provide strong support to the postulate of Audrieth *et al* (1954) that the chloramination of amines resulting in the formation of the corresponding hydrazines, proceed via the intermediate formation of the imide intermediate (NH), as follows:



As described in an earlier work (Jain *et al* 1980) the fixed base (OH^- or OR^-) used abstracts a proton from the chloramine resulting in the formation of the imide molecule which on subsequent reaction with an amine results in the formation of the corresponding hydrazine.

The above mentioned scheme of reactions requires that the minimum concentration of the base (OH^-) should be equal to that of chloramine or amine for the formation of the corresponding hydrazine. However, the yield data (tables 3 and 4) show that there is no formation of either phenylhydrazine or N-aminopiperidine when the reactants are taken in 1:1:1 mole ratio, although when the fixed base concentration is increased, there is ready formation of the respective hydrazines. This may be explained as follows. Although glass wool filters are used in the chloramine generator to check the flow of NH_4Cl from the generator to the reaction vessel, this does not completely prevent NH_4Cl from going to the reaction vessel. This is evident from the white deposition inside the chloramine delivery tube to the reaction vessel. This NH_4Cl then reacts with KOH to form KCl , NH_3 and H_2O . A portion of the fixed base used is thus destroyed by this process. The remaining base possibly would react with chloramine and subsequently with amine to form hydrazine. However, the hydrazine formed, in turn, will get oxidized by the excess chloramine in the absence of the fixed base. As reported earlier, chloramine reacts with the fixed base in preference to hydrazine, but once the fixed base is destroyed it reacts with hydrazine in preference to the respective amine. It, therefore, appears that whatever hydrazine is formed at chloramine:amine:base, 1:1:1, is oxidized by the excess chloramine.

Although the feasibility of the anhydrous chloramine method to synthesis hydrazines in non-aqueous solvents was earlier established in the case of MMH (Jain *et al* 1980) and UDMH (Sisler *et al* 1981) the present study suggests that it be a general method for the synthesis of various hydrazines in anhydrous medium. The formation of water as a reaction product could also be avoided if the fixed base is properly chosen; as shown in the case of MMH (Jain *et al* 1980) synthesis where sodium methoxide was used instead. Sodium methoxide on reacting with chloramine will generate methanol instead of water. It is further conceivable that if the solvent is properly chosen, the recovery of the hydrazines formed could be achieved by a simple distillation method. In the present instance some of the hydrazines such as *p*-tolylhydrazine, β -aminoethylhydrazine and N-aminopyrrolidine, have been synthesised for the first time using the gaseous chloramination method. The synthetic methods available for these and other substituted hydrazines in the literature being highly complicated, the present method suggests an easy way out for their synthesis.

Acknowledgement

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Synthesis of some new *bis*(styryl)sulphones

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Abstract. A series of new *bis*(styryl)sulphones were synthesised by the condensation of various aryl aldehydes with sulphonyldiacetic acid. An attempt has been made to correlate the infrared and proton magnetic resonance spectral data to the configurations of *bis*(styryl)sulphones.

Keywords. *Bis*(styryl)sulphones; configuration; sulphonyldiacetic acid.

1. Introduction

For our studies relating to the synthesis of aryl mono- and dicyclopropyl sulphones, we were interested in preparing a series of new *bis*(styryl)sulphones as intermediates. Only a few methods are found in the literature for the preparation of *bis*(styryl)sulphones. Backer (1953) reported a *bis*(styryl)sulphone by the condensation of sulphonyldiacetic acid with benzaldehyde in the presence of piperidine acetate. Stacey and Harris (1963) synthesised divinyl sulphide by radiation-induced addition of hydrogen sulphide to substituted acetylenes. Aleksiev and Mladenov (1977) reported the synthesis of some divinyl sulphones by the condensation of vinylhalides with styrylsodiumsulphinates. Baliah and Ananthapadmanabhan (1971) reported a few *bis*(styryl)sulphones by extending the procedure of Baliah and Seshapathi Rao (1959) which was originally used for the preparation of α,β -unsaturated sulphones. Otto and Yamamura (1975) reported a few compounds by Backer's method.

2. Results and discussion

A series of new *bis*(styryl)sulphones have been prepared by the condensation of sulphonyldiacetic acid with various aryl aldehydes with fairly high yields (see table 1). In this procedure catalytic amounts of benzylamine and glacial acetic acid were used, instead of piperidine acetate and benzene, as condensing agent and solvent respectively which had been used in the original method.

where Ar =

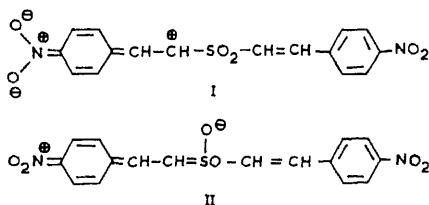
- | | | |
|--|---|---|
| 1 C ₆ H ₅ | 10 3,4-(CH ₃ O) ₂ C ₆ H ₃ | 19 4-CH ₃ OC ₆ H ₄ |
| 2 2-ClC ₆ H ₄ | 11 3,4,5-(CH ₃ O) ₃ C ₆ H ₂ | 20 3,4-(-O-CH ₂ -O)- |
| 3 3-ClC ₆ H ₄ | 12 2-C ₂ H ₅ OC ₆ H ₄ | 21 4-C ₂ H ₅ O, 3-CH ₃ O |
| 4 4-ClC ₆ H ₄ | 13 4-C ₂ H ₅ OC ₆ H ₄ | 22 2-NO ₂ C ₆ H ₄ |
| 5 4-BrC ₆ H ₄ | 14 2-FC ₆ H ₄ | 23 3-NO ₂ C ₆ H ₄ |
| 6 2,4-Cl ₂ C ₆ H ₃ | 15 3-FC ₆ H ₄ | 24 4-NO ₂ C ₆ H ₄ |
| 7 3,4-Cl ₂ C ₆ H ₃ | 16 4-FC ₆ H ₄ | 25 α-naphthyl |
| 8 2,3-(CH ₃ O) ₂ C ₆ H ₃ | 17 2-CH ₃ C ₆ H ₄ | 26 cyclohexyl |
| 9 2,5-(CH ₃ O) ₂ C ₆ H ₃ | 18 4-CH ₃ C ₆ H ₄ | 27 cyclohexene |
| | | 28 3-pyridyl |

Table 1. ArCH=CH-SO₂-CH=CH-Ar.

Compound number	Yield* %	m.p. °C	Formula	Analysis (%)		
				Calculated		Found
				C	H	C
1	20 (25)	99-100 ^a	C ₁₆ H ₁₄ O ₂ S	—	—	—
2	50 (22)	173-174 ^d	C ₁₆ H ₁₂ Cl ₂ O ₂ S	—	—	—
3	74	126-127 ^b	C ₁₆ H ₁₂ Cl ₂ O ₂ S	56.62	3.56	56.82
4	53 (24)	215-216 ^d	C ₁₆ H ₁₂ Cl ₂ O ₂ S	—	—	—
5	48 (18)	230-231 ^d	C ₁₆ H ₁₂ Br ₂ O ₂ S	—	—	—
6	46	165-166 ^a	C ₁₆ H ₁₀ Cl ₄ O ₂ S	45.94	2.41	45.92
7	43	160-161 ^a	C ₁₆ H ₁₀ Cl ₄ O ₂ S	45.94	2.41	45.98
8	25	126-127 ^b	C ₂₀ H ₂₂ O ₆ S	61.53	5.67	62.23
9	29	185-186 ^a	C ₂₀ H ₂₂ O ₆ S	61.53	5.67	61.83
10	64	184-185 ^a	C ₂₀ H ₂₂ O ₆ S	61.53	5.67	61.16
11	33	219-220 ^c	C ₂₂ H ₂₆ O ₈ S	58.66	5.77	58.96
12	31	102-103 ^a	C ₂₀ H ₂₂ O ₄ S	67.02	6.18	67.08
13	33	148-150 ^c	C ₂₀ H ₂₂ O ₄ S	67.02	6.18	67.39
14	45	143-144 ^c	C ₁₆ H ₁₂ F ₂ O ₂ S	62.75	3.92	62.74
15	56	209-211 ^c	C ₁₆ H ₁₂ F ₂ O ₂ S	62.75	3.92	62.71
16	52	185-186 ^c	C ₁₆ H ₁₂ F ₂ O ₂ S	62.75	3.92	63.09
17	49	130-131 ^a	C ₁₈ H ₁₈ O ₂ S	72.46	6.08	72.34
18	63	180-182 ^b	C ₁₈ H ₁₈ O ₂ S	72.46	6.08	72.08
19	60	164-165 ^f	C ₁₈ H ₁₈ O ₄ S	65.43	5.49	65.21
20	42	164-165 ^c	C ₁₈ H ₁₄ O ₆ S	60.32	3.93	60.52
21	24	198-199 ^c	C ₂₂ H ₂₆ O ₆ S	64.18	6.04	64.15
22	56	182-183 ^d	C ₁₆ H ₁₂ N ₂ O ₆ S	53.31	3.35	53.43
23	50	158-160 ^g	C ₁₆ H ₁₂ N ₂ O ₆ S	53.31	3.35	53.8
24	52	292-293 ^h	C ₁₆ H ₁₂ N ₂ O ₆ S	53.31	3.35	53.23
25	33	175-177 ^d	C ₂₄ H ₁₈ O ₂ S	77.80	4.89	77.49
26	56	228-229 ^c	C ₁₆ H ₂₆ O ₂ S	68.11	9.22	68.29
27	46	213-214 ^c	C ₁₆ H ₂₂ O ₂ S	69.07	7.91	68.98
28	34 (30)	147-149 ^a	C ₁₄ H ₁₂ N ₂ O ₂ S	—	—	—

Products recrystallized from (a) 95% ethanol, (b) methanol, (c) *n*-propanol, (d) glacial acetic acid, (e) *n*-butanol, (f) *n*-butanol-95% ethanol mixture, (g) 95% ethanol-acetone mixture and (h) 95% ethanol-ethyl acetate mixture.

The ultraviolet spectra of all these *bis*(styryl)sulphones exhibited a long wavelength band around the 266–360 nm region and some of these compounds show a second band in the region 242–290 nm. Another strong bond with high intensity occurs in the spectra of all these compounds around 200–220 nm region. The long wavelength band around 266–360 nm seems to be due to the conjugation of the sulphone group with the styryl groups. The band near 240 nm may be ascribed to the 'partial' disconjugated styryl ($\text{PhC}=\text{C}-$) chromophore (Klyne 1954). The band appearing in the region 200–220 nm is presumably the *E*-band which occurs for benzene at 180 nm. The high intensity of this band may be due to the greater number of phenyl groups present in the molecule. The absorption maxima for *p*-nitro substituted compounds is found at a longer wavelength (383 nm). The spectral behaviour of the compound can be understood if we assume that electron withdrawal by $-\text{NO}_2$ and $-\text{SO}_2$ groups occurs in opposite directions. The $-\text{NO}_2$ group, being a more powerful conjugating group, seems to have a dominating influence. The result is that the *p*-nitro substituted compound will have a greater contribution towards its excited state from the following structure I, rather than from the structure II.



The infrared spectra of most of these *bis*(styryl)sulphones exhibited a band with medium intensity in the region $1620\text{--}1615\text{ cm}^{-1}$ ($\nu\text{C}=\text{C}$) (Truce and Boudakian 1956; Colthup *et al* 1964) and another strong band in the region $980\text{--}960\text{ cm}^{-1}$ (δCH out-of-plane) (Baliah and Rathinasamy 1971; Seshapathi Rao Naidu and Bhaskar Reddy 1975; Truce *et al* 1960) characteristic of *trans* disubstituted ethylenes. They also displayed bands in the region $1300\text{--}1330\text{ cm}^{-1}$ and $1120\text{--}1130\text{ cm}^{-1}$ which are characteristic of the sulphonyl group (Bavin *et al* 1960; Robinson 1961).

The PMR spectra of all these compounds show the signals for the ethylenic protons as doublets in the region $7.4\text{--}8.4$ and $6.6\text{--}7.2$ ppm. The coupling constants determined for all these compounds gave values from $12\text{--}14$ Hz. These values indicate that all the compounds are *trans* isomers. Mikolajczyk *et al* (1979) has proposed an improved equation of Matter *et al* (1969) to calculate the chemical shifts of vinylic protons. The equation is given below.

$$\delta_{\text{ppm}} = 5.25 + \sum_i Z_i + \sum \Delta S_i^j$$

where Z_i are the respective shielding increments for the substituents (R) in the *gem*, *cis* and *trans* relationship to proton and ΔS_i^j is the increment due to substituent S in the aromatic ring, *i* is the *gem*, *cis* or *trans* position of the substituted aromatic ring with respect to the olefinic proton, *j* is the *para* or *meta* position of the substituent in the aromatic ring. The chemical shifts (δ) for the olefinic protons observed experimentally as well as the values calculated (with the assumption that the protons are in *trans*

Thus the mode of formation, the infrared and proton magnetic resonance spectroscopic studies (coupling constants) confirm that all the *bis*(styryl)sulphones synthesised under the present investigation are *trans* isomers.

3. Experimental

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. The elemental analyses were performed by Dr R D MacDonald, CSIRO, Australia. The ultraviolet absorption spectra were recorded with a Perkin Elmer model-551 spectrophotometer. The infrared spectra were recorded on a Beckman DU 18A spectrophotometer in potassium bromide discs and in nujol mulls. The proton magnetic resonance spectra were recorded in deuteriochloroform solution using Varian XL-100 spectrometer with tetramethylsilane as an internal standard.

3.1 Reagents

The aryl aldehydes were commercially obtained and sulphonyldiacetic acid was prepared following the procedure of Backer (1953).

3.2 General procedure for the condensation of sulphonyldiacetic acid with different aryl aldehydes

A solution of sulphonyldiacetic acid (0.01 mole) in glacial acetic acid (10 ml) was mixed with an aryl aldehyde (0.02 mole) and a catalytic amount (1 ml) of benzylamine and the whole mixture was refluxed for 90 minutes. The reaction mixture was cooled and treated with dry ether (50 ml). Any product separated was collected by filtration and the filtrate was diluted with more ether. The ethereal layer was washed successively with a saturated solution of sodium bicarbonate (15 ml), dilute hydrochloric acid (20 ml) and finally with water. Evaporation of the dried ethereal layer yielded in many cases a solid product of *bis*(styryl)sulphone. However, in some instances a syrupy substance which separated was solidified on treatment with a small amount of methanol or 2-propanol. The relevant data on the compounds synthesised are given in table 1.

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Correlation of x-ray photoelectron spectroscopic core level binding energies with melting point for a series of diamine dihydrochlorides

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Abstract. X-ray photoelectron spectroscopic (xps) and differential thermal analysis (DTA) studies of a series of diamine dihydrochlorides have shown that a linear relationship exists between the N(1s) and Cl(2p_{3/2}) binding energy shifts and the melting points of these salts. A theoretical model is presented to verify this empirical correlation. It is apparent that such binding energy shifts and melting points are also dependent upon intrinsic electronic and bonding features of these salts such as quaternary nitrogen substituent inductive effects, charge delocalisation within the cation, cation-anion interaction and salt hydration.

Keywords. Diamine dihydrochloride; x-ray photoelectron spectrum; differential thermal analysis; melting point; inductive effect; hydration effect.

1. Introduction

With the development of x-ray photoelectron spectroscopy (xps), there have been many applications of this technique to the study of the nitrogen environment in a wide variety of nitrogen compounds. Notable publications in this field have been by Baker and Betteridge (1972), Bakke *et al* (1980), Barber and Clark (1970), Basch and Snyder (1969), Davis *et al* (1970), Fahlman *et al* (1966), Finn *et al* (1971), Hedman *et al* (1969), Hendrickson *et al* (1969), Hollander *et al* (1968), Hollander and Jolly (1970), Jack and Hercules (1971), Jolly and Hendrickson (1970), Nordberg *et al* (1968) and Siegbahn *et al* (1969). A significant aspect of these various studies has been an investigation of correlations of core electron binding energies with: calculated atomic charges, thermodynamic data based on the approximation that the energy of core electron capture by a nucleus is independent of chemical environment, empirical parameters characteristic of directly bonded groups and molecular-orbital-calculated binding energies.

The data of Finn *et al* (1971) and Jack and Hercules (1971) are most relevant to the present study. Finn *et al* (1971) have investigated correlations of empirical N(1s) binding energy shifts for gaseous ammonia, methylamine, dimethylamine and trimethylamine, (i) with nitrogen atomic charges as calculated by the Pauling and CNDO methods, (ii) with thermodynamically estimated N(1s) binding energy shifts and (iii) with N(1s) binding energy shifts derived by the empirical parameter method. Apart from these correlations, a further significant feature of their study is that the N(1s)

binding energies for these compounds, relative to dinitrogen, decrease as the hydrogen atoms of ammonia are successively replaced by methyl groups, which reflects the progressively increasing inductive effect of these substituents. Jack and Hercules (1971) have reported N(1s) binding energy data for a series of tetra-alkylammonium salts $R_4N^+X^-$; R = alkyl or aryl, X = halide. N(1s) binding energies for these quaternary nitrogen compounds were found to be dependent on the nature and size of the R-substituents and on the nature of the halide counter-ion. For salts involving the same R-groups but different X^- anions, a direct correlation exists between the N(1s) binding energy and the electronegativity of X (Jolly 1970, Pauling 1960).

The present study involves the determination of N(1s) and Cl(2p) binding energy shifts for a series of diamine dihydrochlorides and an investigation of a correlation of these shifts with the melting point of these salts.

A melting point broadly represents the temperature at which a crystal lattice converts to a less-ordered or disordered liquid lattice and for a series of structurally related compounds, the variation in melting point reflects the variation in lattice energy within the series. The lattice energy of these diamine dihydrochlorides is primarily determined by the strength of the intrinsic ionic bonding which is in turn dependent on the quaternary nitrogen atomic charge and the degree of interaction of the cation and chloride. The net quaternary nitrogen atomic charge is essentially determined by the nature and number of attached R-substituents and the length of the relevant alkyl chain. R-group steric effects complicate this direct dependency. The net anionic charge depends also on the net quaternary nitrogen atomic charge by virtue of cation-anion interaction. Hence the core level binding energies $E_b^F(N\ 1s)$, $E_b^F(Cl\ 2p)$ and melting point are all related to the magnitude of net atomic charges existing in these compounds. A thermodynamic model is presented to quantify these correlations.

2. Experimental

The diamine dihydrochlorides studied are abbreviated as:

- | | |
|--|---------------------------|
| 1. ethylenediamine dihydrochloride | (en)2HCl |
| 2. N,N'-dimethylethylenediamine dihydrochloride | (Me ₂ en)2HCl |
| 3. N,N'-diethylethylenediamine dihydrochloride | (Et ₂ en)2HCl |
| 4. N,N'-diphenylethylenediamine dihydrochloride | (ϕ_2 en)2HCl |
| 5. 1,3-diaminopropane dihydrochloride | (DAP)2HCl |
| 6. 1,3-diacetyl-1,3-diaminopropane dihydrochloride | (Ac ₂ DAP)2HCl |
| 7. 1,4-diaminobutane dihydrochloride | (DAB)2HCl |
| 8. o-phenylenediamine dihydrochloride | (o-Ph)2HCl |

These salts were prepared according to a procedure previously reported for ethylenediamine dihydrochloride by Roe *et al* (1982) and are characterised by their infrared spectra (table 1) and DTA thermograms (table 2). Infrared spectra in the range 4000–250 cm⁻¹ were obtained on a Perkin-Elmer 457 spectrophotometer, using the KBr disc method with band calibration relative to polystyrene. DTA thermograms were obtained on a Rigaku-Denki, Type 8085 Thermal Analysis System, using platinum

Table 1. (Continued)

ine- rochloride	CH str CH ₂	CH str CH ₃	N ⁺ H str	N ⁺ H def asym.	N ⁺ H def sym.	CH ₂ def scissor	CH ₂ wag	CH ₂ twist	C-C str	C-N str	NH rock	CH rock	NH wag	CNC def	CNH def	C=C str φ
2HCl	3011 s		2751 s	1595 s	1563 s	1383 s	1323 s	1283 s	1218 s	1178 s	1033 s	994 s	762 s	572 s	407 s	1555 s
	2911 s		2661 s						1075 s	1173 s	1007 m	954 s		497 s	357 s	1493 s
	2851 s		2611 s									622 s				1473 s
	2801 s		2561 s									822 m				1433 s
			2496 s													
2HCl			2411 s													
	2941 sb		2791 sb	1548 w	1485 s	1433 s	1403 s	1313 s	1276 s	1116 s	1013 w	896 s	782 s	555 s	1746 s	
	2901 sb		2571 s				1418 s		1213 s	1063 s		872 s		532 s	1661 mb	
	2716 s		2491 s									657 s		437 s		
	2611 s		2451 s											322 s		
2HCl			2411 s													
			2801 sb	1603 s	1503 s			1308 s	1243 s	1183 s	1045 m	842 s	757 s	587 s		1573 s
			2601 sb						1143 s	1081 m	1025 m			534 s		1523 s
			2571 sb							1103 m				522 s		1488 s

s = stretch; asym = asymmetric; sym = symmetric; def = deformation; s = strong; m = medium; w = weak; sh = sharp; b = broad

Table 2. Differential thermal analysis (DTA) data for some diamine dihydrochlorides.

Diamine dihydrochloride	Dehydration endotherm (°C)	Melting endotherm T_m (°C)	Decomposition endotherms (°C)
(en) 2HCl	143 b	339 sh	348 sh, 351 sh, 360 sh, 371 sh
(Me ₂ en)2HCl		246 sh	306 b, 322 sh, 327 sh, 334 sh, 340 sh
(Et ₂ en)2HCl		276 sh	340 sh
(ϕ_2 en)2HCl	72 b	153 sh	200 b
(DAP)2HCl		259 sh	318 sh, 327 sh, 337 sh, 340 sh, 351 sh
(Ac ₂ -DAP)2HCl		252 sh	453 b
(DAB)2HCl	114 b	313 sh	361 sh
(o-Ph)2HCl		214 sh	233 sh, 277 sh

b = broad; sh = sharp.

(1973) using AlK α photons of 1486.6 eV energy and at 10^{-6} – 10^{-7} hPa (torr). All samples were dried in a desiccator over P₂O₅, then pressed onto double-sided adhesive tape and mounted on a double-sided copper sample holder. The metal Cu2p_{3/2} electron binding energy (932.5 eV) (Barr 1978) served as the calibrant level for all core level binding energies relative to the spectrometer Fermi Level. Tests for surface charging effects of these non-conducting samples were carried out by varying the intensity of the incident x-rays. No binding energy corrections were found necessary. Measured binding energies of spectral features were also measured to ± 0.3 eV (Liesegang *et al* 1984).

3. Results and discussion

Detailed infrared data for the diamine dihydrochlorides are presented in table 1 and assignments are relative to those for ethylenediamine dihydrochloride. The presence of a C–N⁺H₃ stretching vibration at 2044 cm⁻¹ as reported by Waldron (1953) is not confirmed by Powell (1960) or by the present study. For all salts, the C–H and N–H stretching bands are generally broad and are associated with submaxima. Powell (1960) has attributed these features to strong intermolecular hydrogen-bonding between the quaternary ammonium cations. The infrared spectra summarised in table 1 essentially characterise the diamine dihydrochlorides studied.

DTA data for these diamine dihydrochlorides are given in table 2. In general, for each salt, a melting endotherm and a series of decomposition endotherms are exhibited; (en)2HCl, (DAB)2HCl and (ϕ_2 en)2HCl additionally exhibit single dehydration endotherms. The thermal stability of these salts is reflected by the temperature corresponding to the first decomposition endotherm; and thus for the series, the lower and upper limits of thermal stability correspond to (ϕ_2 en)2HCl and (Ac₂-DAP)2HCl respectively. Increase of the alkyl chain length between the quaternary nitrogen atoms or change of R-groups attached to these atoms produces no systematic variation in temperatures corresponding to the decomposition endotherms; and thus there is no obvious correlation of the thermal stability of these salts with chemical structure.

Table 3. E_b^F (N 1s) and E_b^F (Cl 2p) data (± 0.3 eV) for some diamine dihydrochlorides.

Diamine Dihydrochloride	E_b^F (N 1s) (eV)	E_b^F (Cl 2p) (eV)	ΔE_b^F (N 1s) (eV) ^a	ΔE_b^F (Cl 2p) (eV) ^b
(en)2HCl	397.3	193.0	-9.6	-14.8
	s 396.2	213.7	-10.7	+5.9
(Me ₂ en)2HCl	397.4	192.6	-9.5	-15.2
	s 396.2	213.4	-10.7	+5.6
(Et ₂ en)2HCl	397.1	193.0	-9.8	-14.8
		211.3		+3.5
(ϕ_2 en)2HCl	398.3	191.7	-8.6	-16.1
		212.3		+4.5
(DAP)2HCl	397.6	193.2	-9.3	-14.6
		212.1		+4.3
(Ac ₂ -DAP)2HCl	397.9	192.6	-9.0	-15.2
		212.1		+4.3
(DAB)2HCl	397.2	192.0	-9.7	-15.8
	s 395.9	215.1	-11.0	+7.3
(o-Ph)2HCl	396.2	193.1		-14.7
		212.8	-10.7	+5.0

^arelative to E_b^F (N 1s) in KNO₃ = 406.9 eV (Jack and Hercules 1971); ^brelative to E_b^F (Cl 2p) in Cl₂ = 207.8 eV (Bakke *et al* 1980); s = shoulder.

(en)2HCl, (DAB)2HCl and (Me₂en)2HCl at E_b^F = 396.2, 395.9 and 396.2 eV respectively. Nordberg *et al* (1968) have reported that under xps conditions, ammonium salts decompose to yield hydrogen chloride. Therefore it is assumed here that (en)2HCl, (DAB)2HCl and (Me₂en)2HCl partially decompose to yield the corresponding free amine and HCl, the former being responsible for the N(1s) shoulders in the xps spectra of these salts. Further, all salts exhibit a broad set of secondary Cl 2p peaks, separated from the main Cl 2p peak by about 20 eV. These structures are assigned to a range of electron energy loss processes of a type described for example by Battye *et al* (1976).

The electron withdrawing effect of phenyl is apparent from the relatively high E_b^F (N 1s) of (ϕ_2 en)2HCl compared to the corresponding E_b^F (N 1s) for (Me₂en)2HCl and (Et₂en)2HCl.

The relatively low E_b^F (N 1s) for (o-Ph)2HCl compared to that of (en)2HCl is a reflection of π -electron delocalisation in (o-Ph)2HCl which tends to increase the electron density on the quaternary nitrogen atoms and decrease E_b^F (N 1s).

Some correlations of xps data with melting points of these salts will now be presented. In general, the salts with R-substituents attached to the quaternary nitrogen atoms have lower melting points than the corresponding unsubstituted diamine dihydrochlorides. Thus for (DAP)2HCl and (Ac₂-DAP)2HCl, the melting points are 259 and 252°C respectively and the -I inductive effect of acetyl is reflected in the xps data for (Ac₂-DAP)2HCl relative to that for (DAP)2HCl. A similar relationship between melting point and xps data emerges for the compounds: (en)2HCl, (Me₂en)2HCl, (Et₂en)2HCl and (ϕ_2 en)2HCl.

to atoms (l) in terms of the corresponding partial charges q_m, q_l , the bond length r_{lm} and an extra-atomic relaxation energy term R^{ea} :

$$\Delta E_b^F(m) = K_m q_m + \sum_{l \neq m} \frac{K_l q_l}{r_{lm}} - R^{ea} \quad (1)$$

where $E_b^F(m)$ is relative to a free atom m and K_m, K_l are constants. The term $\sum_{l \neq m} (K_l q_l / r_{lm})$ is the molecular potential term which according to Siegbahn *et al* (1969) and Fadley *et al* (1968) is analogous to the Madelung Potential for a solid. In the case of diamine dihydrochlorides, q_m is the charge on the quaternary nitrogen atoms, q_l is the charge on the chloride ions and r_{lm} is the internuclear distance between these ions. Equation (1) indicates that binding energy shifts are critically dependent on the parameters q_m, q_l and r_{lm} and hence, to correlate xps data for diamine dihydrochlorides with corresponding melting points, it is necessary to consider the thermodynamic properties of these salts in terms of the same parameters.

For diamine dihydrochlorides, the sequential phase changes shown in figure 1 may be assumed to occur on heating.

ΔH_{fus} , ΔH_{vap} and ΔH_{dec} are the fusion, vaporisation and decomposition enthalpies of the salt respectively. Huheey (1978) has defined the molar lattice energy U of an ionic solid as:

$$U = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} + U_{ip} + U_c, \quad (2)$$

where U_{ip} and U_c are the respective energies associated with ion-pair and cluster-ion formation in the gas phase. U_{ip} and U_c are essentially dependent upon the polarising power of the component ions and since diamine hydrochlorides are associated with large cations and a relatively large anion, both U_{ip} and U_c are small. Further, diamine dihydrochlorides decompose in the liquid phase prior to boiling and hence

$$\Delta H_{\text{fus}} \gg |\Delta H_{\text{vap}} + U_{ip} + U_c| \quad (3)$$

or

$$U = c_1 \Delta H_{\text{fus}} \quad (4)$$

where c_1 is a constant. ΔH_{fus} , by Trouton's rule, is directly related to the melting point T_m and hence:

$$U = c_1 T_m \Delta S_{\text{fus}}. \quad (5)$$

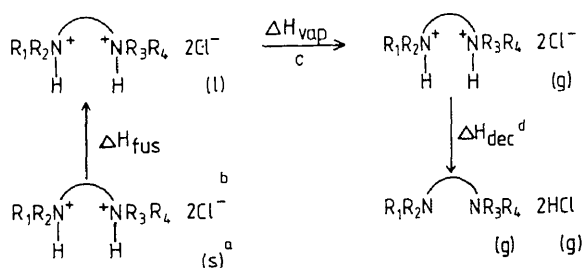


Figure 1. Enthalpy Diagram for a diamine dihydrochloride: a, thermodynamic state: (s) solid, (l) liquid, (g) gas; b, chemical structural formula for a diamine dihydrochlorides,

ΔS_{fus} , the entropy of fusion, is dependent on the relative order associated with the solid and liquid phases and since the diamine dihydrochlorides studied have closely related chemical structures, ΔS_{fus} is assumed to be constant for the series and hence:

$$U = c_2 T_m \quad (6)$$

with c_2 constant.

U is given by the Kapustinskii equation (Huheey 1978):

$$U = \frac{c_3 q_m q_l}{r_{lm}} \quad (7)$$

with c_3 constant.

Combining (7) with (6) gives:

$$q_m = c_4 (r_{lm}/q_l) T_m \quad (8)$$

with c_4 constant.

Combining (8) with (1) gives:

$$\Delta E_b^f(m) = c_5 (r_{lm}/q_l) T_m + \sum_{l \neq m} K_l q_l / r_{lm} - R^{ea} \quad (9)$$

with c_5 constant.

(9) may be conveniently rewritten in the form:

$$\Delta E_b^f(m) = AT_m + B, \quad (10)$$

where

$$A = c_5 r_{lm} / q_l \quad (11)$$

and

$$B = \sum_{l \neq m} [K_l q_l / r_{lm}] - R^{ea} \quad (12)$$

may be viewed as pseudo-constants.

It is apparent that if a linear relationship between ΔE_b^f and T_m exists, then ΔE_b^f is inherently more dependent on melting point than on all of the other variables in (9).

ΔE_b^f (N 1s) vs T_m and ΔE_b^f (Cl 2p) vs T_m plots for the diamine dihydrochlorides studied are shown in figures 2 and 3 respectively. The respective negative and positive slopes are consistent with (9) since the slope sign is determined by the sign of q_l .

It is appropriate to comment on those diamine dihydrochlorides, the xps T_m data for which correspond to deviation from the 'best-fit' lines of figures 2 and 3. If it is assumed that these deviations result primarily from 'abnormal' A and B values, then an explanation is possible based on operative inductive effects, although other factors such as abnormal fusion entropies may contribute. Inductive effects fundamentally define the magnitude of q_l and hence A and B and thus the discussion of deviations is confined to an assessment of these variables, duly recognising that the variations in R^{ea} are assumed to be small within the series of diamine dihydrochlorides studied and that the proposed theoretical model is approximate.

(*o*-Ph)2HCl is clearly the most abnormal and exhibits deviation in both cases. Charge delocalisation in the cation tends to decrease the positive charge on the quaternary nitrogen atoms and increase the negative charges q_l , thereby increasing the charge on chlorine (figure 2) or decreasing this charge in the context of figure 3. Steric hindrance between the two adjacent quaternary nitrogen groups tends to increase r_{lm} . If it is assumed that the substitution in the cation is in the form of a phenyl group, then the

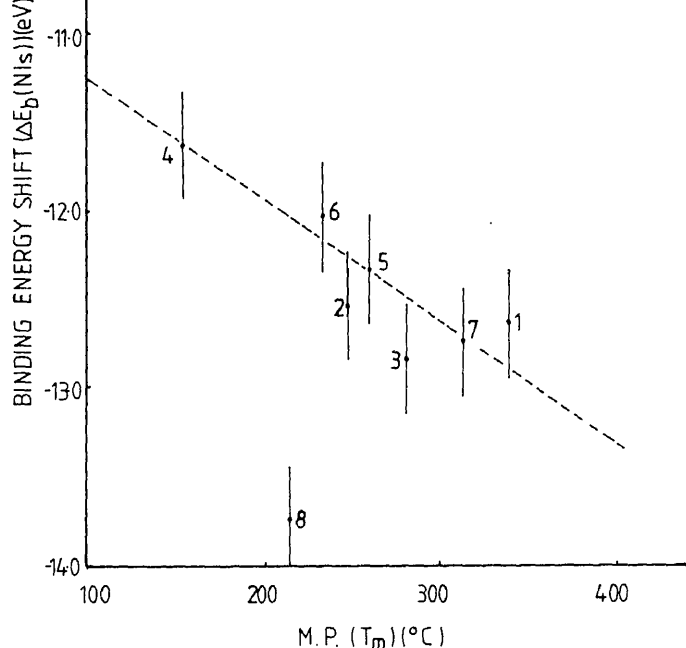


Figure 2. The variation of N1s binding energy shift with T_m for diamine dihydrochlorides. 1. (en)2HCl 2. (Me₂en)2HCl 3. (Et₂en)2HCl 4. (φ₂en)2HCl 5. (DAP)2HCl 6. (Ac₂DAP)2HCl 7. (DAP)2HCl 8. (o-Ph)2HCl.

for (o-Ph)2HCl is a decreased A and B (figure 2) or conversely, an increased A and B (figure 3).

(Et₂en)2HCl exhibits a lower A than (en)2HCl (figure 1). The +I inductive effect of ethyl tends to reduce the charge on the quaternary nitrogen atoms and thereby increases q_I and decreases r_{Im} , resulting in a decrease in both A and B . However, within the limits of experimental error, (en)2HCl and (Me₂en)2HCl are on the 'best fit' line (figure 2) which suggests that the inductive effect of R-group substituents is not the only influence on q_I .

The deviation of (en)2HCl, (DAP)2HCl and (DAB)2HCl (figure 3) may be a reflection of hydration of (en)2HCl and (DAB)2HCl relative to anhydrous (DAP)2HCl. Hydration tends to effect the environment of Cl⁻ to a greater extent than that of quaternary nitrogen, and hence is more apparent in the E_b^f (Cl 2p) data than in the corresponding E_b^f (N 1s) data.

Apart from (o-Ph)2HCl, the deviations shown in figures 2 and 3 relate to different diamine dihydrochlorides which essentially reflect the differential influence of inductive and steric effects and hydration on the N and Cl environments in these compounds.

It is relevant to discuss the xps data presented in table 4. The compounds listed are

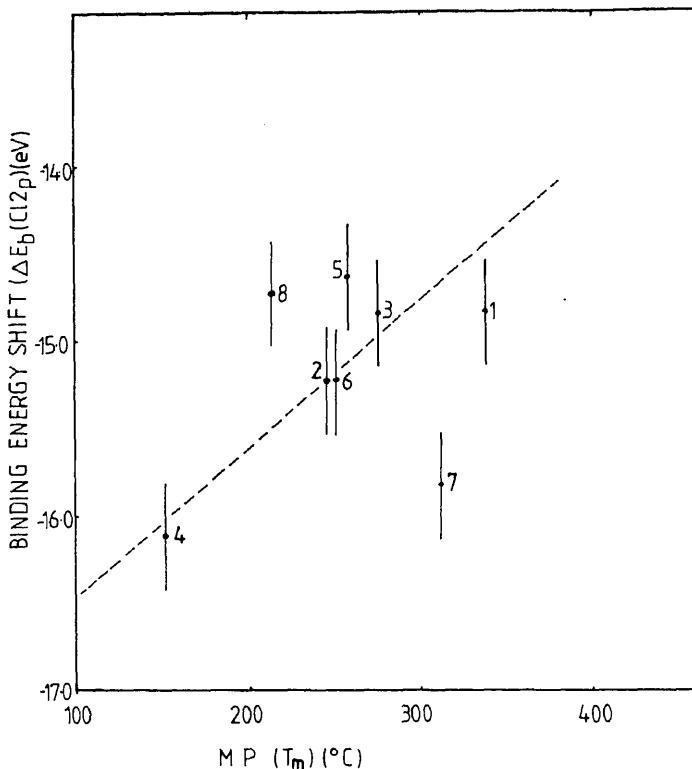


Figure 3. The variation of Cl2p binding energy shift with T_m for diamine dihydrochlorides. 1. (en)2HCl 2. (Me₂en)2HCl 3. (Et₂en)2HCl 4. (ϕ_2 en)2HCl 5. (DAP)2HCl 6. (Ac₂DAP)2HCl 7. (DAB)2HCl 8. (o-Ph)2HCl.

either amines, amine salts or tetraalkyl ammonium salts and hence are structurally related to diamine dihydrochlorides. The xps data for these compounds are readily interpreted in terms of inductive effects. With respect to the primary amines $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, increase of the alkyl chain length decreases the $E_B^F(\text{N } 1s)$ in accordance with an increased alkyl group inductive effect. With reference to $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ and $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}$, replacement of one H atom on the former amine with a propyl group also decreases $E_B^F(\text{N } 1s)$ as a consequence of an increased inductive effect of propyl versus hydrogen. With respect to the tetraalkyl ammonium halides, $(\text{CH}_3)_4\text{NF}$, $(\text{CH}_3)_4\text{NCl}$ and $(\text{CH}_3)_4\text{NBr}$, as the electron withdrawing effect of the halide decreases, $E_B^F(\text{N } 1s)$ decreases. With reference to $(\text{CH}_3)_4\text{NI}$, the extraneous $E_B^F(\text{N } 1s)$ peak at 402.30 eV is explained by Nordberg *et al* (1968) as due to decomposition of the salt to trimethylamine.

Formation of piperidine hydrochloride from piperidine increases $E_B^F(\text{N } 1s)$ as a direct consequence of an increased positive charge on the ring nitrogen and the electron withdrawing inductive effect of chloride ion. With respect to $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ and $(\text{CH}_3)_4\text{N}^+\text{O}^-$ the exchange of Cl^- by O^- has the effect of increasing $E_B^F(\text{N } 1s)$ as a

Table 4. A summary of literature xps data for selected nitrogen compounds.

Compound	E_F^F (N 1s) (± 0.3 eV)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2^a$	398.1
 NH^a	397.8
 $\text{N}^+\text{H}_2\text{Cl}^{-a}$	400.4
$(\text{CH}_3\text{CH}_2)_3\text{N}^+\text{HCl}^{-a}$	400.4
$(\text{CH}_3)_4\text{N}^+\text{Cl}^{-a}$	401.5
$(\text{CH}_3)_4\text{N}^+\text{O}^{-a}$	402.2
$(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{I}^{-a}$	397.1
	402.3
$(\text{CH}_3)_4\text{N}^+\text{F}^{-b}$	401.2
$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2^c$	405.0
$(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH}^c$	404.5
$(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{ClO}^{-d}$	401.1
$(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{ClO}_4^{-d}$	400.5
$(\text{CH}_3\text{CH}_2)_3\text{N}^+\text{HBr}^{-d}$	399.7
$(\text{CH}_3)_4\text{N}^+\text{Br}^{-d}$	400.7

^aNordberg *et al* (1968); ^bBaker and Betteridge (1972);^cBakke *et al* (1980); ^dJack and Hercules (1971).

4. Conclusion

N 1s and Cl 2p binding energies for a series of diamine dihydrochlorides have been interpreted in terms of the electronic environments of nitrogen and chlorine in these salts. The xps data have also been correlated with the melting points of these salts and deviations from the empirical linear relationship have been explained in terms of structural features such as variable ionic character in the N-Cl bond of the salt, hydration effects and non-systematic inductive effects. xps data for some related compounds as reported in the literature are also discussed in relation to similar data for diamine dihydrochlorides.

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Comparative studies on the absorption and emission characteristics of isomeric chlorobenzonitriles

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Abstract. Absorption, fluorescence and phosphorescence characteristics of isomeric chlorobenzonitriles have been studied and similarities and differences in these have been noted and compared with those of analogous compounds reported in the literature. The variations in absorption spectral characteristics have been explained and the correlation between the dipole moments of the molecules and the energy of the para isomers has been elucidated. Analyses of the phosphorescence data have led to the conclusion that internal heavy atom spin-orbit coupling effect is important in the chlorobenzonitriles and that the radiative and nonradiative rates from their triplet states may be reasonably rationalized on this basis.

Keywords. Isomeric chlorobenzonitriles; dipolemoment; charge transfercharacter; internal heavy atom effect; radiative and nonradiative rates.

Introduction

Carsey *et al* (1979) investigated from both experimental and computational points of view the variation in the absorption and emission properties of para-disubstituted benzenes with the nature of the substituents, one being an electron donor and the other an electron acceptor. Similar, but less detailed, studies in the case of *ortho*- and *meta*-substituted benzenes were reported by Findley *et al* (1979). On the basis of these studies they proposed that the energy, $E(^1L_a)$, of the 1L_a state of these molecules may be used to parametrize the charge transfer (CT) character in their 1L_a state and that, in the case of the *para*-compounds, the $E(^1L_a)$ energy is a useful and convenient gauge of their molecular polarity in their ground and excited singlet and triplet states. According to Carsey *et al* (1979) the general trends of variation in the luminescence characteristics, as systematized by them, are in good agreement with the experimental results of Lui and McGlynn (1975a, b and c, 1978). Recently such studies in isomeric chlorobenzonitriles, which are weak polar compounds, have been reported by Maiti *et al* (1984). The present investigation is an extension of this to isomeric chlorobenzonitriles. The purpose of this study is, firstly, to test the validity of the conclusions of Carsey *et al* (1979) for these weakly polar substituted benzonitriles as regards the correlation between the energy of the 1L_a state and the solvent shift of the 1L_a absorption band, and secondly, to find out how the radiative and nonradiative properties of the phosphor-

escence emitting triplet state of the chlorobenzonitriles are modified relative to those of the fluoro substituted analogues.

With these objects in mind, detailed investigations on the absorption, fluorescence and phosphorescence properties of the isomeric chlorobenzonitriles in the vapour phase, in polar and nonpolar solvents, and at different temperatures have been carried out. The results obtained and their discussion form the subject of the present paper.

2. Experimental

Pure samples of three isomeric chlorobenzonitriles, obtained from Fluka A.G. (Switzerland), were sublimed several times under reduced pressure till no impurity was detected with GLC (Hewlett-Packard Model 5730A) using flame ionisation detector in conjunction with the column ucw 982, twenty inches in length. Solvents ethanol and methylcyclohexane were of spectrograde quality from E. Merck (W. Germany) and they were distilled under reduced pressure before use each time. De-oxygenated solutions of the chlorobenzonitriles of $\approx 10^{-4}$ M concentration were prepared by the usual freeze and thaw-cycles. Details of the experimental methods for recording absorption, fluorescence and phosphorescence spectra and the procedure for the determination of fluorescence and phosphorescence quantum yields are the same as described in our previous paper (Maiti *et al* 1984). The accuracy of measurement is also the same as given there.

3. Results

3.1 Absorption spectra

Like all other substituted benzonitriles belonging to the D-Ph-A system, where D and A are respectively electron donor and electron acceptor substituents and Ph is the

Table 1. Absorption spectral data of chlorobenzonitriles in the vapour phase and in solution at room temperature.

Molecule	Phase	1L_a band system		1L_b band system		$E(^1L_a) - E(^1L_b)$ (cm^{-1})
		$\nu_{0,0}$ (cm^{-1})	f	$\nu_{0,0}$ (cm^{-1})	f	
<i>o</i> -Chlorobenzonitrile	Vapour	43 497		35 026		8471
	MCH	42 181	0.166	34 712	0.021	
	EtOH	42 813	0.216	34 772	0.024	
<i>m</i> -Chlorobenzonitrile	Vapour	44 209		35 149		9060
	MCH	42 813	0.134	34 772	0.030	
	EtOH	42 813	0.127	34 480	0.025	
		(42 920)		(34 780)		
<i>p</i> -Chlorobenzonitrile	Vapour	42 409		36 166		6243
	MCH	41 653	0.254	35 451	0.013	
	EtOH	41 653	0.290	35 514	0.015	
		(42 640)		(35 710)		

phenyl ring, the isomeric chlorobenzonitriles exhibit, in the vapour phase and in solutions, two systems of absorption bands in the near UV region designated, respectively, ${}^1L_a \leftarrow {}^1A$ and ${}^1L_b \leftarrow {}^1A$ under Platt notation. Symmetrywise, for the *ortho*- and *meta*-isomers (C_s -point group) both these transitions are ${}^1A' \leftarrow {}^1A'$, while for the para isomer (C_{2v} point group) the former transition is ${}^1A_1 \leftarrow {}^1A_1$ and the latter ${}^1B_2 \leftarrow {}^1A_1$. In subsequent descriptions 1A , 1L_b and 1L_a denote respectively ground and first and second excited states in the singlet manifold of these molecules. The relevant data on the absorption spectral characteristics of the three isomers are presented in table 1, while vibrational assignments of their spectra in ethanol glass at 77 K are given in table 2.

In all cases, the spectra due to the *ortho*- and *meta*-isomers are similar but different

Table 2. Vibrational analysis of the absorption and fluorescence spectra of chlorobenzonitriles in ethanol at 77 K.

Absorption			Fluorescence		
$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	assignment
<i>o</i> -Chlorobenzonitrile					
			(34 250)		
34 712 (s)	0	0,0	34 622 (w)	0	0,0
35 101	389	0+389	34 320 (w)	302	0-302
35 768 (s)	1056	0+1056	33 533 (w)	1089	0-1089
36 889 (ms)	2177	0+2 × 1056	32 432 (w)	2190	0-2 × 1089
37 689 (w)	2977	0+3 × 1056			
38 326 (w)	3614	0+389+3 × 1056			
38 975	4263	0+4 × 1056			
39 336	4624	0+389+4 × 1056			
Ground state vibration frequencies ^a ; 391, 1031, 1132 cm^{-1}					
<i>m</i> -Chlorobenzonitrile					
			(34 480)		
34 783 (s)	0	0,0	34 745 (w)	0	0,0
35 111 (s)	328	0+328	34 431 (ms)	314	0-314
35 842	1059	0+1059	33 745 (ms)	1000	0-1000
36 900 (w)	2117	0+2 × 1059	33 385	1360	0-314-1000
37 951	3168	0+3 × 1059	32 670 (w)	2042	0-2 × 1000
Ground state vibration frequencies ^a ; 302, 995, 1076, 1192 cm^{-1}					
<i>p</i> -Chlorobenzonitrile					
			(34 250)		
35 640 (s)	0	0,0	35 736 (ms)	0	0,0
36 386 (ms)	746	0+746	35 437	299	0-299
36 686 (ms)	1046	0+1046	34 622 (s)	1114	0-1114
37 164 (s)	1524	0+1524	33 488 (w)	2288	0-2 × 1114
37 477	1837	0+746+1046			
37 867	2227	0+746+1524			
38 230 (w)	2590	0+1046+1524			
34 748	3108	0+2 × 1524			
Ground state vibration frequencies ^a ; 302, 780, 1086, 1177, 1198, 1596 cm^{-1}					

s—strong, m—medium, w—weak; ^a Green and Harrison (1976); Values in parentheses are from Carsey

from that of the *para*-isomer, the f -values of the 1L_a and 1L_b bands of the *para* isomer are higher than the corresponding values of the parent benzonitrile molecule, the energy gap $E({}^1L_a) - E({}^1L_b)$ changes in the order $m > o > p$ and its value is the least in the *para*-compound.

The absorption spectra of the three isomers in ethanol glass at 77 K show sufficient vibrational structures (table 2). In each of the *ortho*- and *meta*-isomers short progression involving 3 or more quanta of the excited state frequency 1050 cm^{-1} is observed. In contrast, such progression is absent in the spectrum of the *para*-isomer in which combination bands are more prominent.

3.2 Fluorescence spectra

Though the fluorescence intensities of all the three chlorobenzonitriles in ethanol (EtOH) and methylcyclohexane (mch) glasses at 77 K are small, some vibronic structures are observed in the spectrum of each of the compounds. The analysis of the bands in the ethanol glass spectrum is presented in table 2. It is seen from the table that in each of these molecules the position of the fluorescence band origin is very nearly coincident with that in absorption in the same medium at 77 K. From the vibrational assignment in table 2, it is also found that besides one or two other vibrational modes, two quanta of vibration involving 1089 cm^{-1} in the *ortho*, 1000 cm^{-1} in the *meta*- and 1114 cm^{-1} in the *para*-compound are present in the respective spectra.

3.3 Phosphorescence emissions

Unlike fluorescence emission, the phosphorescence intensities of the compounds in both EtOH and mch glass are moderately strong and show greater vibrational features. These data together with the assignments are presented in table 3. It is found that in all cases many ground state fundamental frequencies occur, and of these the frequency $\approx 1600\text{ cm}^{-1}$ corresponding to $\nu(\text{C}=\text{C})$ vibration of the phenyl ring is very prominent and occurs upto two quanta of excitation. Besides, in the spectra of each of *meta*- and *para*-isomers a strong band with frequency shift $\sim 2300\text{ cm}^{-1}$ attributable to the $\nu(\text{C}\equiv\text{N})$ vibration in these molecules is observed, while bands at a separation of $\sim 1150\text{ cm}^{-1}$, attributable to $\nu(\text{C}-\text{CN})$ vibration, are seen in the spectra of *ortho*- and *para*-chlorobenzonitriles.

3.4 Other luminescence characteristics

Some of the luminescence characteristics of the isomeric chlorobenzonitriles are collected in table 4 and for comparison the data for tolunitriles (Maiti *et al* 1984) and fluorobenzonitriles (Lui and McGlynn 1975a) are included. The following trends in the variations of these characteristics between the different triads and among the members of the same triad are discernable.

The singlet-triplet ($S_1 - T_1$) separation increases in the order $p > m > o$ and is the largest for the *para*-compound. This is similar to that observed in the tolunitriles (Maiti *et al* 1984) and in fluorobenzonitriles and cyanoanisoles (Lui and McGlynn 1975a, b). The fluorescence intensity in the isomeric chlorobenzonitriles is very small and in fact,

Table 3. Vibrational analysis of phosphorescence spectra of chlorobenzonitriles.

MCH-glass at 77 K			EtOH glass at 77 K		
cm^{-1}	$\Delta\nu(\text{cm}^{-1})$	Assignment	$\nu(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Assignment
<i>o</i> -Chlorobenzonitrile (25 970) [26 378]					
291 (<i>ms</i>)	0	0,0	26 317 (<i>s</i>)	0	0,0
509 (<i>ms</i>)	232	0—232	26 084 (<i>s</i>)	233	0—233
775 (<i>ms</i>)	516	0—516	25 807	510	0—510
1150 (<i>w</i>)	1141	0—1141	25 121 (<i>w</i>)	1196	0—1196
1691 (<i>s</i>)	1600	0—1600	24 730 (<i>vs</i>)	1587	0—1587
1555 (<i>w</i>)	2136	0—516—1600	24 555 (<i>ms</i>)	1762	0—233—1587
1630 (<i>vw</i>)	2661	0—2 × 516—1600	24 220 (<i>m</i>)	2097	0—510—1587
Ground state vibration frequencies ^a ; 207, 505, 1132, 1197, 1584 cm^{-1}					
<i>m</i> -Chlorobenzonitrile (26 320) [26 041]					
291 (<i>ms</i>)	0	0,0	26 395 (<i>ms</i>)	0	0,0
709	212	0—212	26 188 (<i>ms</i>)	207	0—207
658 (<i>s</i>)	633	0—633	25 763 (<i>s</i>)	632	0—632
286 (<i>w</i>)	1005	0—1005	25 418 (<i>w</i>)	977	0—977
741 (<i>ms</i>)	1550	0—1550	24 829 (<i>s</i>)	1566	0—1566
981 (<i>vs</i>)	2310	0—2310	24 600	1795	0—207—1566
767 (<i>s</i>)	2524	0—212—2310	24 024 (<i>vs</i>)	2371	0—2371
392 (<i>ms</i>)	2899	0—633—2310	23 392 (<i>ms</i>)	3003	0—2 × 1566
		0—2 × 1550			0—632—2371
637 (<i>m</i>)	3654	0—633—2 × 1550			
Ground state vibrational frequencies ^a ; 197, 677, 995, 1587, 2233 cm^{-1}					
<i>p</i> -Chlorobenzonitrile (25 840) [26 229]					
1009 (<i>ms</i>)	0	0,0	26 136 (<i>w</i>)	0	0,0
783	226	0—226	25 832 (<i>ms</i>)	304	0—304
634 (<i>ms</i>)	375	0—375	25 324	812	0—812
197	812	0—812	25 009 (<i>s</i>)	1127	0—1127
899 (<i>s</i>)	1110	0—1110	24 600 (<i>vs</i>)	1536	0—1536
442 (<i>vs</i>)	1567	0—1567	24 199 (<i>ms</i>)	1937	0—304—1536
089 (<i>ms</i>)	1920	0—812—1110	23 789 (<i>s</i>)	2347	0—2346
					0—812—1536
661 (<i>s</i>)	2348	0—2348	23 474 (<i>m</i>)	2662	0—1127—1536
330 (<i>ms</i>)	2679	0—1110—1567	23 048	3088	0—2 × 1536
890 (<i>m</i>)	3119	0—2 × 1567			
Ground state vibration frequencies ^a ; 248, 302, 350, 780, 1090, 1171, 1596, 2236 cm^{-1}					

—strong, *m*—medium, *w*—weak, *v*—very; ^aGreen and Harrison (1976); Values in parentheses are from Parsey *et al* (1979) (in EPA) and in square brackets are from Asahi and Hirota (1982).

The phosphorescence quantum yield (Φ_p) also decreases in the same order but the variation between the different triads is not as large as for Φ_f . In the fluorobenzonitriles Maiti *et al* (1984) and tolunitriles (Lui and McGlynn 1975a) the values of Φ_p and as well of Φ_p/Φ_f are the largest for the *para*-isomer whereas in the chlorobenzonitriles this occurs in the case of the *meta*-compound. On the other hand, though phosphorescence

Table 4. Fluorescence and phosphorescence quantum yields, lifetimes, intersystem crossing, radiative and nonradiative phosphorescence rates and other parameters of substituted benzonitriles.

Molecule (at 77 K)	Solvent	Φ_F	Φ_P	Φ_P/Φ_F	τ_P sec	$S_1 - T_1$ cm^{-1}	$K_{ISC} \times 10^{-6}$ (sec^{-1})	K_P (sec^{-1})	K_P^w (sec^{-1})	$\frac{K_P(\text{Cl})}{K_P(\text{F})}$
<i>o</i> -Chlorobenzonitrile	MCH	0.004	0.054	13.8		8037				
	EtOH	0.003	0.088	31.4		8331				
	EPA ^a			10.6	0.38		68.3	0.232	2.40	3.01
<i>m</i> -Chlorobenzonitrile	MCH	0.005	0.120	35.3		8421				
	EtOH	0.003	0.236	47.2		8421				
	EPA ^a			18.7	0.47		24.2	0.505	1.66	7.29
<i>p</i> -Chlorobenzonitrile	MCH	0.004	0.101	26.6		9600				
	EtOH	0.003	0.107	34.5		9642				
	EPA ^a			16.8	0.15		42.2	0.725	5.96	4.80
<i>o</i> -Tolunitrile	EtOH ^b	0.36	0.24	0.67	3.40	8506		0.18		
<i>m</i> -Tolunitrile	EtOH ^b	0.51	0.23	0.45	4.60	8795		0.10		
<i>p</i> -Tolunitrile	EtOH ^b	0.36	0.33	0.92	3.80	9332		0.14		
<i>o</i> -Fluorobenzonitrile	EtOH ^c	0.51	0.093	0.18	2.43	8700		0.077	0.33	
<i>m</i> -Fluorobenzonitrile	EtOH ^c	0.54	0.082	0.15	2.60	8900		0.068	0.31	
<i>p</i> -Fluorobenzonitrile	EtOH ^c	0.24	0.23	0.96	2.05	9300		0.15	0.33	

^aCarsey *et al* (1979); ^bMaiti *et al* (1984); ^cLui and McGlynn (1975a).

3.5 Dipole moment and solvent effect

The dipole moments of the isomeric chlorobenzonitriles in the 1L_a and 1L_b states have been calculated from the solvent shift data in MCH solution at room temperature in the same way as in tolunitriles (Maiti *et al* 1984). The ground state dipole moments are taken from published literature (Wesson 1948) and the volume of the molecule (a^3) has been taken to be $25A^3$ in all cases. The relevant data for the chlorobenzonitriles together with those for some other benzonitriles are given in tables 5 and 6. The solvatochromic shifts in the position of the 1L_a -band of these molecules in ethanol are shown in table 6 and the computed values of $\mu^2(^1L_a) - \mu^2(^1A)$ are included therein.

Table 5. Solvent shifts and dipole moments of substituted benzonitriles.

Molecule	Solvatochromic shift* $\Delta\nu(\text{cm}^{-1})$ in ethanol at room temperature		Dipole moment (Debye)		
	1L_a band	1L_b band	Ground state (1A)	First excited state (1L_b)	Second excited state (1L_a)
<i>o</i> -Chlorobenzonitrile	684	254	4.73	5.37	6.80
<i>m</i> -Chlorobenzonitrile	1396	409	3.38	4.34	6.25
<i>p</i> -Chlorobenzonitrile	756	652	2.50	4.79	3.43
<i>o</i> -Fluorobenzonitrile ^a	1170	310			
<i>m</i> -Fluorobenzonitrile ^a	1170	380			
<i>p</i> -Fluorobenzonitrile ^a	800	60	2.64		
<i>o</i> -Tolunitrile ^b		631	3.95	5.07	
<i>m</i> -Tolunitrile ^b	1708	543	4.25	5.21	6.31
<i>p</i> -Tolunitrile ^b	1181	310	4.40	5.23	5.43
Benzonitrile ^b	1463	410	4.10	4.81	5.83

* $\Delta\nu = \nu_{00}(\text{gas}) - \nu_{00}(\text{solution}) \text{ cm}^{-1}$; ^aLui and McGlynn (1975a); ^bMaiti *et al* (1984).

Table 6. Comparative data on some parameters of 1L_a state of *para*-substituted benzonitriles.

Molecule parameters	Benzonitrile ^a	Paratolu- nitrile ^a	Parafluoro- benzonitrile ^b	Parachloro- benzonitrile
$\mu(^1A)$ Debye	4.10	4.40	2.64	2.50
$\mu(^1L_b)$ "	4.81	5.23		4.79
$\mu(^1L_a)$ "	5.83	5.43		3.43
$E(^1L_a) \text{ cm}^{-1}$	44740	43185	44100	42409
$E(^1L_a) - E(^1L_b) \text{ cm}^{-1}$	8240	7981	7500	6243
Solvatochromic shift in ethanol cm^{-1}	1463	1181	800	756
$\mu^2(^1L_a) - \mu^2(^1A)$	17.17	10.30		5.51

4. Discussion

4.1 Energies and oscillator strengths

Similarities in the absorption characteristics of the *ortho*- and *meta*-isomers and their differences from those of the *para*-substituted benzonitriles have already been noted in §3. To provide a qualitative rationalization for these observations, the methods of linear combination of configuration wave functions (Suzuki 1967) for the description of the π electronic states of the D-Ph-A system are considered. These states are expressed in terms of linear combinations of the locally excited (LE) configurations, corresponding to α , p , β and β' bands of the phenyl ring and the symmetric and antisymmetric CT configurations arising from the entities D^+-Ph^-A , $D-Ph^+-A^-$ and D^+-Ph-A^- . The degree of mixing of the configurations is governed by the energies of the configurations, corrected for the inductive effects of the substituents, and the Hamiltonian matrix elements between pairs of these configurations. It may be noted that in the C_{2v} -symmetry (benzonitrile and the *para* compounds) the lower energy state (1B_2) will be composed of linear combinations of the LE (α), LE(β') and antisymmetric CT configurations while the upper excited state (1A_1) will comprise LE(p), LE(β) and the symmetric CT configurations. In the C_s -symmetry (*ortho* and *meta*) both the lower and upper excited states will be linear combinations of all the configurations. Though no definite statements may be made as to the energies of the excited states and the proportion of each configuration in them without actual calculations, it is apparent that because of the mixing of fewer number of configurations, the energy of the lower excited state (1B_2) of benzonitrile and its *para*-derivatives is expected to be higher than that of the *ortho*- and *meta*-isomers. Also the mixing of all the configurations in the excited states in the *ortho*- and *meta*-isomers provides qualitative explanation for the similarities in their absorption characteristics.

In all these cases the f -value of $^1L_b \leftarrow ^1A$ transition mainly depends on the weight of LE(β) and LE(β') configurations in the linear representation of the first excited state, because transition to these states in the phenyl ring has the highest f -value, while those to the LE(α) and LE(p) states are nil. The contributions to f -value from the CT configurations are negligible for the donors considered in the present investigation. Since in the *para*-compounds only the LE(β') contributes, their f -values are smaller than that in the other two isomers. Findley *et al* (1979) presented explanations for the above mentioned observed features in a similar manner. However, according to them, the increase in the f -value of the two transitions in the *ortho*- and *meta*-compounds are due to such CT configurations for which 1CT dipole transition moments are considerable.

4.2 Polarities of the ground, 1L_b and 1L_a excited states of *para*-substituted benzonitriles and their correlation with the energy of 1L_a state

According to Carsey *et al* (1979) the energy of the $^1L_a \leftarrow ^1A$ band of *para*-D-Ph-A compounds is a useful gauge of the polarity of the molecules in the ground and excited singlet and triplet states. They also proposed a correlation between $E(^1L_a)$ and the magnitude of solvatochromism of the 1L_a band in polar solvents and contended that this shift should be proportional to $\mu(^1L_a) - \mu(^1A)$. From the relevant data for the *para*-compounds including benzonitrile, collected in table 6, it is seen that there is no regular

in agreement with the conclusions of Carsey *et al* (1979) and might be due to the fact that these authors used computed dipole moment values instead of the values derived from experimental data. As regards their other observation that for a fixed acceptor (nitrile) group the values of $E(^1L_a)$ and the energy gap $E(^1L_a) - E(^1L_b)$ decrease with increasing donor capability, the data in table 6 show clearly that $E(^1L_a) - E(^1L_b)$ rather than $E(^1L_a)$ decreases smoothly as the donor capability of the substituent increases. From the same table it is seen that the solvatochromic shift follows the same trend as the band gap value, and there is a rough proportionality between the two. Furthermore, the shift decreases with decrease in the value of $\mu^2(^1L_a) - \mu^2(^1A)$. This is partly in agreement with the conclusion of Carsey *et al* (1979).

4.3 Character of the excited states of chlorobenzonitrile molecules

It has already been noted in §3.2 that in each of these molecules the position of the fluorescence band origin is almost coincident with that in absorption implying a mirror image symmetry. Since fluorescence is the reverse process of absorption, the fluorescence emitting state is the same as the first excited π, π^* state in the singlet manifold, and hence is a 1L_b state. As regards the character of the phosphorescence emitting triplet state, it is noted that the phosphorescence lifetimes of the chlorobenzonitrile molecules are about 0.5 sec (Carsey *et al* 1979) and that the phosphorescence spectra comprise mainly of ring vibrational modes. From these facts it is reasonably concluded that the emitting triplet state in each of these molecules is of the π, π^* type. From theoretical considerations Carsey *et al* (1979) and Findley *et al* (1979) concluded that this state may be designated as 3L_a .

4.4 Phosphorescence lifetime of chlorobenzonitriles and nonradiative rates

From table 4 it is seen that the measured phosphorescence lifetime (τ_p) of the chlorobenzonitriles (Carsey *et al* 1979) is about an order smaller than that of the tolunitriles (Maiti *et al* 1984) and fluorobenzonitriles (Lui and McGlynn 1975a). The smallness of the τ_p values clearly points to the well known heavy atom spin-orbit coupling effect on the phosphorescence lifetime. A theoretical explanation of this effect has been given by McGlynn *et al* (1969), who from simplified considerations showed that in a system of analogous planar aromatic molecules with different halogen atoms as substituents, like the 1-halonaphthalenes, the ratio of the phosphorescence radiative lifetime (τ_p^0) for the chlorine substituted member to that of the member with a fluorine substituent is given by

$$\tau_p^0(\text{F})/\tau_p^0(\text{Cl}) = K_p(\text{Cl})/K_p(\text{F}) = (\xi_{\text{Cl}}/\xi_{\text{F}})^2 = 4.66,$$

where $K_p = \tau_p^{0-1}$ is the phosphorescence radiative rate constant ξ is the atomic spin orbit coupling factor and the suffixes Cl and F refer to chlorine and fluorine atoms respectively. Asahi and Hirota (1982) discussed the applicability of the concepts derived in the case of the halonaphthalenes to the halobenzonitriles and pointed out that the decay rate constants would increase with ξ^2 values in going from lighter to heavier

due to either a large nonradiative rate constant (K_S) from the first singlet state to the ground state, or large intersystem crossing rate constant (K_{ISC}). Determination of K_{ISC} values would have been most appropriate, but unfortunately this has not been possible. Instead the validity of the second alternative has been assumed, and the values of K_{ISC} , K_p and K_p^{nr} of chlorobenzonitriles have been computed under the assumption $K_S = 0$ as in the case of the isomeric tolunitriles (Maiti *et al* 1984) and fluorobenzonitrile (Lui and McGlynn 1975a). The values are shown in table 4.

It is seen from these data that $K_p(\text{Cl})/K_p(\text{F})$ has the values 3.01, 7.29 and 4.80 for the *ortho*, *meta* and *para*-isomeric pairs respectively of the chloro- and fluorobenzonitriles. The agreement appears to be very good for the *para*-isomers and tolerable for the other two pairs of molecules. Though much reliance need not be placed on the quantitative agreement, it is reasonable to assume a qualitative validity of internal heavy atom effect. This by implication indicates that the nonradiative rate constant K_S is really small and K_{ISC} is large.

A large K_{ISC} value for the chlorobenzonitriles would imply a large phosphorescence quantum yield (Φ_p) for them, but from table 4 it is seen that the magnitude of Φ_p in these molecules is of the same order as that in the fluorobenzonitriles (Lui and McGlynn 1975a). This indicates that a large part of the excitation transferred to the emitting triplet state of these molecules is lost through nonradiative processes. In fact, the computed data in this table show that the phosphorescence radiative rate constant (K_p) in the chlorobenzonitriles is about an order higher than that of fluorobenzonitriles, and so are the nonradiative rate constants (K_p^{nr}). Since the moment of the $T_1 \rightarrow S_0$ radiative transition is due to mixing of the excited states of the molecule in the singlet manifold with the emitting triplet state through spin-orbit coupling, the higher value of K_p in the chloroderivative is certainly attributable to the larger spin-orbit coupling matrices in them as compared to that in the fluoroderivatives.

The reasons for the larger nonradiative loss from the triplet to the ground state in the chlorobenzonitriles are not apparent at once. In the course of investigation of the internal heavy atom effect on the T_1 states Najbar *et al* (1983) found that the nonradiative losses due to chlorine atom substitution in the aromatic molecules of monochloroquinolines and naphthalenes are affected. Such changes depend on many factors, of which the most evident are the changes of the spin-orbit coupling. Though no quantitative calculations have been performed in the present case, the observations may be rationalized, at least qualitatively, mainly on the basis of difference in the spin-orbit coupling factor in the chloro- and fluorobenzonitrile molecules.

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Excess thermodynamic properties of the binary mixtures of ethylenediamine with isomeric butanols

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Abstract. Isothermal vapour-liquid equilibrium data at 333.15 K and excess molar volumes of mixing at 298.15 K for the binary mixtures of ethylenediamine with isomeric butanols were measured over the entire mole fraction range. The values of molar excess free energy, G_m^E , and excess volumes, V_m^E , are negative for all the four systems, indicating strong specific interactions between two unlike molecules. The branching of the alkyl chain of alcohol also affects the excess properties considerably.

Keywords. Excess thermodynamic properties; binary mixtures; amine-alcohol interactions; dilution dilatometer; excess volumes; excess free energy.

1. Introduction

In continuation of the earlier studies (Datta Choudhary 1976; Pradhan 1979, 1981) in this laboratory on the excess thermodynamic properties of the binary mixtures of associated liquids viz. alcohol-amine systems, the present work was undertaken to understand the diamine-alcohol interactions.

In this communication, the isothermal vapour-liquid equilibrium data at 333.15 K and the excess molar volumes, V_m^E , at 298.15 K for the four binary systems of ethylenediamine (EDA) with *n*-, *iso*-, *sec*-, and *t*-butanol (V_m^E of EDA-*t*-butanol at 299.15 K) have been reported.

Vapour liquid equilibrium data is not available for any of the above systems, whereas excess volumes at 303.15 K for ethylenediamine with *n*-, *iso*- and *sec*-butanol have been reported by Rao *et al* (1981, 1982). In the present studies, a continuous dilution dilatometer has been used to obtain V_m^E data at 298.15 K. This method is better and more accurate than the batch method (Kumaran and McGlashan (1977)).

2. Experimental

2.1 Materials

Analytical reagent grade butanols were fractionally distilled twice over a NaOH-AgNO₃ mixture using a meter long column packed with glass helices. Ethylenediamine was similarly purified over metallic sodium. All the compounds were stored over activated molecular sieves (4A). The purity of the compounds was checked by comparing the densities with literature values (Reddick and Bunger 1970; Timmermans 1950).

2.2 Apparatus and procedure

2.2a Vapour-liquid equilibrium: The vapour-liquid equilibrium data at 333.15 K were obtained using a modified Jones-Colburn recirculating still (Ammer *et al* 1956). The values of system pressures determined were accurate to within ± 0.01 mm. Barometric and gravitational corrections were applied to the measured values of system pressures. The liquid and vapour compositions of the solutions were determined by densitometric analysis.

The liquid phase activity coefficients (γ) were calculated by means of the relations (Datta Choudhary 1976):

$$\gamma_i = (Py_i/P_i^s x_i) \exp \{ [(V_i - B_{ii})(P_i^s - P) + \delta_{12}(1 - y_i)^2 P] / RT \}, \quad (1)$$

where $i = 1, 2$ (1 = ethylenediamine and 2 = butanol); $\delta_{12} = 2B_{12} - B_{11} - B_{22}$; x_i , y_i are the liquid and vapour mole fractions respectively; P is the solution pressure, P_i^s is vapour pressure of pure component (atm); V is liquid molar volume ($\text{cm}^3 \text{mol}^{-1}$); B is the second virial coefficient ($\text{cm}^3 \text{mol}^{-1}$); R = gas constant and T is the temperature. Here δ_{12} was taken as zero.

The second virial coefficients (B) for alcohols were calculated using Tsonopoulos equation (Tsonopoulos 1974) and for ethylenediamine by the Pitzer Curl equation (Pitzer and Curl 1957). The values of B are listed in table 1 along with the liquid molar volumes (V) at 333.15 K. The values of B do not affect the γ values much at lower pressures.

The molar excess free energy, G_m^E , was calculated by the relation.

$$G_m^E (\text{J} \cdot \text{mol}^{-1}) = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2). \quad (2)$$

2.2b Excess molar volumes: The excess volumes, V_m^E , at 298.15 K were measured by a dilution dilatometer based on the design of Kumaran and McGlashan (1977). The necessary calibrations were done at 298.15 K, before the dilatometer was assembled. The proper working of the apparatus was tested by measuring V_m^E of a benzene-cyclohexane system at 298.15 K.

The data on excess volumes were obtained at 298.15 K for all the systems except for EDA-t-butanol at 299.15 K. The thermostat temperature was controlled to ± 0.01 K and the excess volumes were reproducible to $\pm 0.002 \text{ cm}^3 \text{mol}^{-1}$. Compression corrections were taken into account.

Table 1. Second virial coefficients (B) and liquid molar volume (V) of pure compounds at 333.15 K.

Compounds	B ($\text{cm}^3 \text{mol}^{-1}$)	V ($\text{cm}^3 \text{mol}^{-1}$)
<i>n</i> -Butanol	-2360	95.2
<i>iso</i> -Butanol	-2634	96.4
<i>sec</i> -Butanol	-2288	96.0
<i>t</i> -Butanol	-1740	99.7

The values of G_m^E are plotted against x_1 , the liquid mole fraction of EDA, in figure 1. The thermodynamic consistency of the experimental data was checked by the equal area method (Herington 1952). All the systems were found to be thermodynamically consistent within 4–5%. The higher deviations may be due to the imperfect nature of the vapour phase.

The G_m^E vs x_1 plot shows that the excess free energy is negative throughout the concentration range, indicating strong specific interactions due to the hydrogen bonding between unlike molecules. The G_m^E values decrease with the branching of alcohol. They are in the order:

$$iso > n > sec \geq t\text{-butanol}.$$

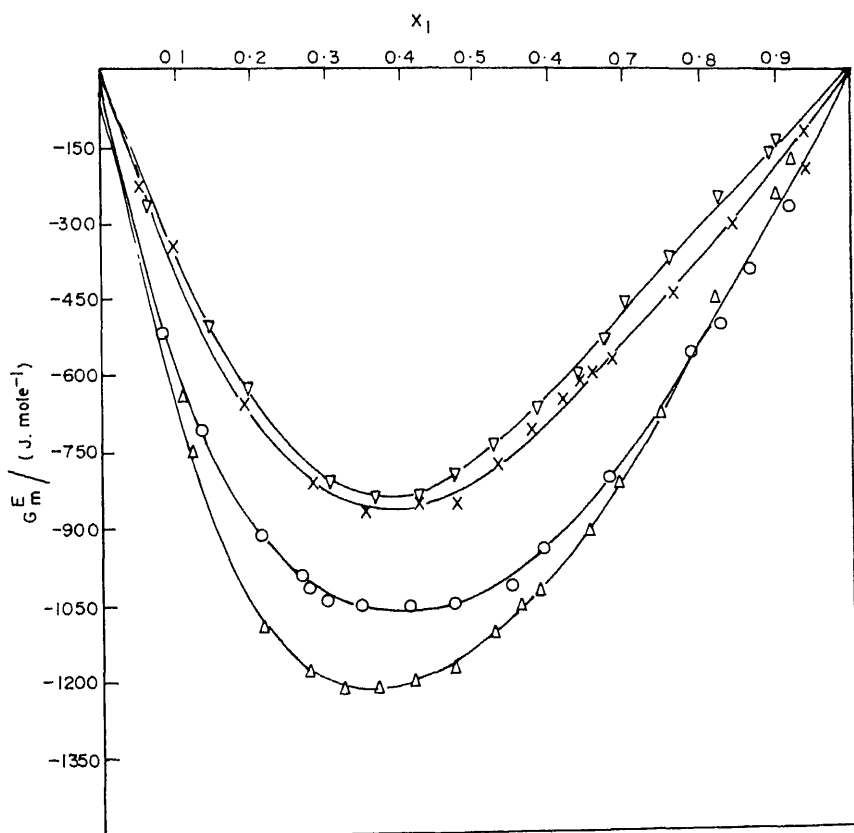


Figure 1. The G_m^E versus x_1 curves for (○) ethylenediamine (1) + *n*-butanol (2); (△) ethylenediamine (1) + *iso*-butanol (2); (×) ethylenediamine (1) + *sec*-butanol (2); (▽) ethylenediamine (1) + *t*-butanol (2) at 333.15 K; (—) values calculated from (3).

3.2 Excess molar volumes

Excess volumes are obtained at 298.15 K for all the systems and the results are plotted in figure 2, as a function of x_1 . The excess volumes are negative over the entire mole fraction range, indicating complex formation between two unlike molecules. The results can be explained in terms of bond breaking and making, and structural effects. Both the ethylenediamine and the butanols are self-associated due to the formation of N-H...N and O-H...O type hydrogen bonds in their pure state (Vinogradov and Linnel 1971). The experimental V_m^E values being negative indicate that O-H...N bonds result from stronger specific interactions between compounds with dissimilar molecules than those between similar molecules. This is in agreement with views

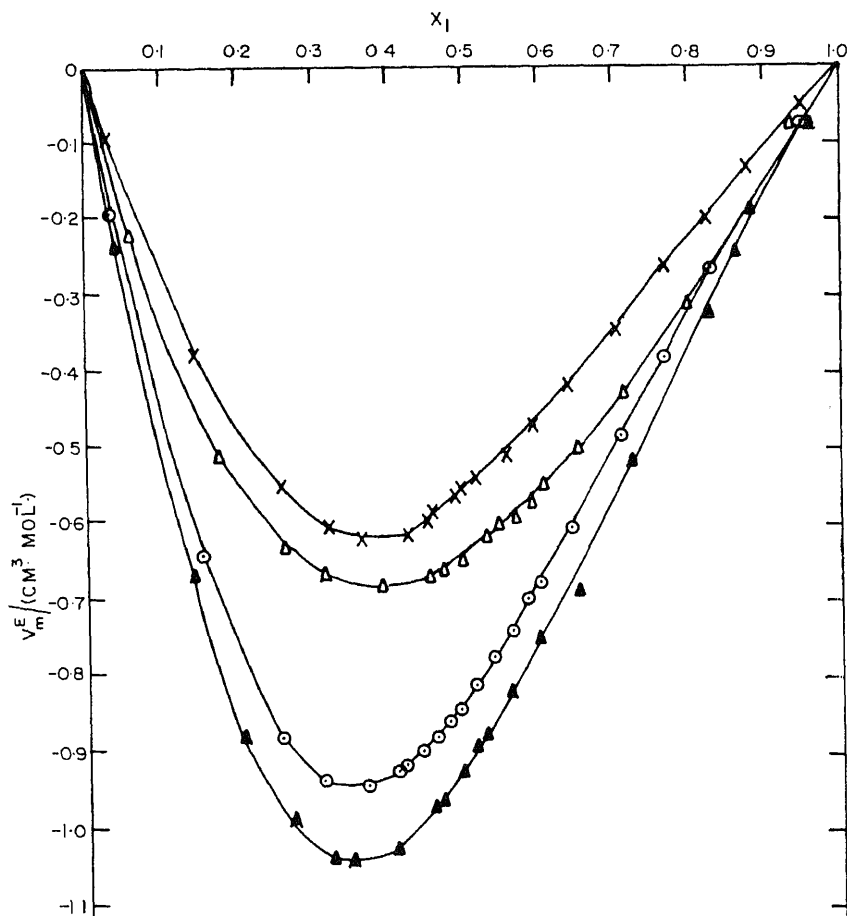


Table 2. Values of the parameters A_0, A_1, A_2, A_3 of (3) along with standard deviations $\sigma(G_m^E)$ and $\sigma(V_m^E)$.

System	A_0	A_1	A_2	A_3	σ
For G_m^E (at 333.15 K)					
EDA (1) + <i>n</i> -butanol (2)	-4038.9	1557.3	-1591.7	684.7	18.0
EDA (1) + <i>iso</i> -butanol (2)	-4644.1	2391.0	-329.4	610.3	19.0
EDA (1) + <i>sec</i> -butanol (2)	-3196.3	1778.0	-161.1	-697.3	15.0
EDA (1) + <i>t</i> -butanol (2)	-3071.9	1933.5	180.4	-171.8	12.0
For V_m^E (at 298.15 K)					
EDA (1) + <i>n</i> -butanol (2)	-3.3161	2.5912	-0.2653	-0.4393	0.004
EDA (1) + <i>iso</i> -butanol (2)	-3.6822	2.7915	-0.2981	-0.5325	0.008
EDA (1) + <i>sec</i> -butanol (2)	-2.2300	1.5124	0.1391	-0.4235	0.004
EDA (1) + <i>t</i> -butanol (2)	-2.5414	1.2471	-0.3847	0.0680	0.004

expressed by other authors (Rao and Naidu 1981; Domonkos and Ratkovics 1982; Fernandez *et al* 1983).

The size, shape and symmetry of the molecules also affects the excess property. The values of V_m^E fall in the order:

$$iso- > n- > t- > sec\text{-butanol}.$$

This trend is consistent with excess free energy results. It seems from the results that the interactions between unlike molecules are stronger at about 0.33 mole fraction of ethylenediamine. The ethylenediamine molecule contains two NH_2 groups and can simultaneously bind with two molecules of alcohol.

This indicates the possibility of the formation of 1:2 complexes between ethylenediamine and alcohol molecules.

3.3 Correlation of data

The G_m^E and V_m^E data were least square fitted to a polynomial equation of the type:

$$X_m^E = x_1 x_2 \sum_{n=0}^3 A_n (x_1 - x_2)^n \quad (3)$$

where $X_m^E = V_m^E$ or G_m^E ; x_1 = mole fraction of ethylenediamine; A_n = least square constant.

The values of constants obtained by the least square method using an ICL-1904S computer, are reported in table 2, along with the standard deviation σ .

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***Ab initio* studies on the electronic structure of some substituted benzenes**

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Abstract. *Ab initio* Molecular orbital (MO) calculations with the 4-31G, 6-31G (split valence) and 6-31G* (split valence + polarized) basis sets have been carried out on monofluorobenzene and *o*-, *m*-, *p*-difluorobenzenes to study ground state properties such as orbital energies, gross orbital charges, net atomic charges and dipole moments. The redistribution of charges consequent to excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) has also been calculated. The results so obtained have been compared and discussed in the light of semi-empirical calculations and available experimental observations. The present study suggests the intermingling of the σ and π orbitals; however, the highest occupied and lowest unoccupied molecular orbitals are of π -symmetry indicating that most of the chemical and spectroscopic properties are controlled by π -electrons. It is also noted that the substituent fluorine is a weak π -donor and a strong σ -attractor. On exciting an electron from HOMO to LUMO it is observed that certain reactions may proceed through excited states. Though, in general, the semi-empirical and *ab initio* methods predict the same trend, the latter should be applied in order to explore the finer details of the chemical properties for the molecules considered in the present investigation.

Keywords. Orbital energies; gross orbital charges; net atomic charges; dipole moments; excited states.

1. Introduction

A knowledge of the electronic structure of substituted benzenes is of basic importance for a deeper understanding of their reactivities and spectral properties. Therefore, the study of their electronic structures has received much attention at every stage of the development of the molecular orbital theory. The method developed by Pariser-Parr and Pople (PPP) provides a fairly satisfactory description of both the ground and the excited state properties of substituted benzenes (Misra and Rai 1970, 1972). Though several features of the electronic structure can be understood with the help of these calculations, several equally important aspects cannot be satisfactorily explained. These latter aspects include contributions from the so-called inductive effects of the substituent and correspond to the changes in the σ -electron framework of the compounds. Therefore, an extensive application of the all valence electrons molecular orbital method was carried out on substituted benzenes (Yadav *et al* 1972a, b, 1973a, b, 1975). The general agreement between both the π -electrons method and the all valence electrons molecular orbital approximation is encouraging. However, the approximate all valence electrons method also did not reproduce all the experimental results since the parameters suitable for some properties were not exactly suitable for the other

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indices. Also different sets of parameters were suggested in a particular approximation by different workers (Del Bene and Jaffee 1968). Furthermore, different approximate methods (Pople and Beveridge 1970) were available with varying degrees of reliability and success. Moreover some workers in the field are of the opinion that semi-rigorous procedures are no longer adequate for molecular electronic structure calculations (Kaufman 1979).

The fourth generation in computers has made available quantum chemical programs which include all electrons of the system wherein all electron integrals were evaluated analytically. This prompted several investigators to apply *ab initio* methods to some substituted benzenes (Hehre *et al* 1972b; Binning and Sando 1980; Boggs *et al* 1982). The computations due to Hehre *et al* (1972b) were carried out on a STO-3G basis set for a fixed geometry whereas Binning and Sando (1980) applied a double zeta contracted gaussian basis set. Recently several workers (Boggs *et al* 1982) and (Nagi-Felsobuki *et al* 1982) in their separate communications have reported structures of some substituted benzenes with 4-21G and STO-3G, 4-31G basis sets respectively. None of these studies included the systematic applications of double zeta plus polarised basis sets to the electronic structure of these molecules. It was therefore thought worthwhile to apply gaussian series of programs (Binkley *et al* 1977, 1983) at split valence and split valence plus polarized basis sets to some substituted benzenes as we have a long standing interest in quantum chemical calculations on these molecules (Misra and Rai 1970, 1972; Yadav *et al* 1972a, b, 1973a, b, 1975) hoping that the inclusion of polarised functions will improve the quality of the results.

The main purpose of this study is to extend our calculations upto the *ab initio* level and to provide reliable and fairly accurate information on the electronic structures of these molecules. The present paper deals with studies on mono-fluorobenzene and isomeric di-fluorobenzenes. The results will be discussed in the light of available experimental and other non- and semi-empirical results.

2. Method of calculation

All the molecules have been taken as planar, the bond angles as 120° and the bond lengths C-C, C-H and C-F as 1.397, 1.084 and 1.350 Å respectively. The calculations were performed on a CYBER 175 computer using Gaussian-76 Program (Binkley *et al* 1977) with 4-31G basis set (Ditchfield *et al* 1971) of 160 and 176 primitive gaussians contracted to 73 and 80 basis functions, a 6-31G basis set (Hehre *et al* 1972a) of 174 and 192 primitive gaussians contracted to 73 and 80 basis functions and Gaussian-82 Program (Binkley *et al* 1983) with 6-31G* basis set (Hariharan and Pople 1973) of 216 and 240 primitive gaussians contracted to 115 and 128 basis functions for the mono-fluorobenzene and the di-fluorobenzenes respectively. A calculation of the redistribution of charges has also been made on exciting an electron from HOMO to LUMO, the elements of the density matrix are changed according to the equation:

$$P'_{\mu\nu} = 2 \sum_i^{\text{occ}} C_{\mu i} C_{\nu i} - (C_{\mu})_{\text{HOMO}} (C_{\nu})_{\text{HOMO}} + (C_{\mu})_{\text{LUMO}} (C_{\nu})_{\text{LUMO}}$$

The elements of the newly constructed density matrix multiplied by their respective overlap integrals give the new Mulliken's population from which the charges on each

3. Results and discussions

3.1 Orbital energies

The energies for five highest occupied and five lowest unoccupied molecular orbitals and their symmetry types have been presented in table 1.

The general observation regarding the σ - π separability in the present non-empirical study and our earlier semi-empirical investigation is almost the same. However, some noticeable differences are present. For instance, the second HOMO is of π -symmetry in all the molecules of the present study whereas in INDO and CNDO/2 calculations (table 1), they are of σ -symmetry in monofluorobenzene and *p*-difluorobenzene. Furthermore, in *p*-difluorobenzene the third and fourth HOMO have π and σ symmetries respectively in 6-31G* but their symmetries are reversed in 4-31G and 6-31G methods. It is also interesting to mention that in all the *ab initio* methods the third and fourth HOMO have nearly the same energy though their symmetries are σ and π respectively. Thus *ab initio* results very clearly suggest that σ and π orbitals could have similar energies. The same mixing appears also in non-empirical (Clementi 1967) and semi-empirical studies on nucleic acid bases (Prettre and Pullman 1968).

The symmetry of the HOMO, an indication of the symmetry of the ionized species, is found to be of π -symmetry in all the methods. This is in agreement with the usual assumption that the excitation and ionization mechanisms are mainly controlled by π -electrons in conjugated and aromatic molecules.

The ionization potential, the energy of the HOMO, obtained from the improved basis set 6-31G* is in excellent agreement with the experimental value (table 1). The energy difference between HOMO and LUMO decreases from 4-31G to 6-31G to 6-31G*. The examination of atomic orbital coefficients reveals that it is not possible to speak of fluorine lone-pairs in the context of the present calculations since they appear to be strongly mixed with other atomic orbitals in molecular orbitals.

3.2 Gross-orbital charges

The following conclusions can be drawn from the study of the orbital populations of carbon, fluorine and hydrogen atoms.

1. The assumption of sp^2 hybridization on the carbon atoms implies the charge population described as $2s^1$, $2p_x^1$, $2p_y^1$ and $2p_z^1$. The present calculations do show a similar distribution of charges except on the carbon to which the substituent fluorine is attached. There is a deficit of about $\cdot 85 e$ (approximately the same in all calculations) in the $2s$ atomic orbitals of all the carbon atoms as compared to a free carbon atom. This deficit which represent promotion from a $2s$ to a $2p$ orbit is explained as being due to the ensuing energy gains from sp^2 hybridization.

2. It is clear that the accepted concept of fluorine being a strong σ -attractor and a weak π -donor (back donation effect) is well borne out by the detailed charge distribution pattern in all the molecules. The amount of π -charges donated to the ring

Table 1. Orbital energies (a.u.)† for five highest occupied and five lowest unoccupied MO.

Molecules	Methods MO	Present calculation					Earlier calculation (Semi-empirical)			
		4-31G	6-31G	6-31G*	Experi- mental	PPP**	CNDO/2***	INDO***		
Monofluoro- benzene	HOMO	-0.527 σ	-0.528 σ	-0.526 σ		—	—	—	—	
		-0.508 π	-0.509 π	-0.501 π		—	—	—	—	
		-0.501 σ	-0.503 σ	-0.501 σ		-0.481 π	-0.526 π	-0.507 π		
		-0.351 π	-0.352 π	-0.345 π		-0.378 π	-0.516 σ	-0.500 σ		
		-0.341 π	-0.342 π	-0.333 π	-0.340 ^a	-0.367 π	-0.490 π	-0.467 π		
	LUMO	+0.132 π	+0.127 π	+0.131 π	-0.354 ^b	-0.028 π	+0.130 π	+0.148 π		
		+0.143 π	+0.139 π	+0.145 π		-0.023 π	+0.136 π	+0.156 π		
		+0.225 σ	+0.225 σ	+0.228 σ		+0.085 π	+0.242 σ	+0.245 π		
		+0.279 σ	+0.279 σ	+0.284 σ		—	—	—		
		+0.294 σ	+0.293 σ	+0.298 σ		—	—	—		
o-difluoro- benzene	HOMO	-0.550 σ	-0.551 σ	-0.546 σ		—	—	—		
		-0.528 σ	-0.530 σ	-0.524 σ		-0.473 π	-0.533 π	-0.517 π		
		-0.519 π	-0.520 π	-0.509 π		-0.371 π	-0.525 π	-0.505 π		
		-0.365 π	-0.366 π	-0.355 π		-0.359 π	-0.488 π	-0.464 π		
		-0.355 π	-0.356 π	-0.344 π	-0.341 ^a	-0.023 π	+0.116 π	+0.133 π		
	LUMO	+0.118 π	+0.114 π	+0.122 π		-0.018 π	+0.122 σ	+0.140 π		
		+0.129 π	+0.125 π	+0.136 π		+0.088 π	+0.244 σ	+0.218 π		
		+0.211 σ	+0.210 σ	+0.216 σ		—	—	—		
		+0.274 σ	+0.273 σ	+0.278 σ		—	—	—		
		+0.289 σ	+0.286 σ	+0.297 σ		—	—	—		
		-0.552 σ	-0.554 σ	-0.547 σ		—	—	—		
		-0.532 σ	-0.533 σ	-0.528 σ		—	—	—		

<i>m</i> -difluoro- benzene	HOMO	-0.518 π	-0.519 π	-0.509 π	-0.471 π	-0.537 σ	-0.523 σ
		-0.366 π	-0.367 π	-0.356 π	-0.370 π	-0.523 π	-0.305 π
		-0.355 π	-0.357 π	-0.344 π	-0.360 π	-0.494 π	-0.471 π
		+0.118 π	+0.114 π	+0.123 π	-0.023 π	+0.116 π	+0.123 π
		+0.129 π	+0.126 π	+0.137 π	-0.018 π	+0.123 π	+0.142 π
	LUMO	+0.219 π	+0.218 σ	+0.223 σ	+0.088 π	+0.236 σ	+0.210 σ
		+0.281 σ	+0.279 σ	+0.286 σ	—	—	—
		+0.287 σ	+0.286 σ	+0.294 σ	—	—	—
		-0.586 σ	-0.589 σ	-0.580 σ	—	—	—
		-0.518 π	-0.519 π	-0.513 σ	—	—	—
<i>p</i> -difluoro- benzene	HOMO	-0.517 σ	-0.519 σ	-0.508 π	-0.471 π	-0.543 π	-0.526 π
		-0.371 π	-0.372 π	-0.361 π	-0.375 π	-0.519 σ	-0.503 σ
		-0.350 π	-0.351 π	-0.338 π	-0.355 π	-0.477 π	-0.453 π
		+0.122 π	+0.108 π	+0.115 π	-0.026 π	+0.112 π	+0.129 π
		+0.135 π	+0.132 π	+0.143 π	-0.015 π	+0.126 π	+0.144 π
	LUMO	+0.219 σ	+0.219 σ	+0.223 σ	+0.088 π	+0.240 π	+0.219 π
		+0.269 σ	+0.269 σ	+0.276 σ	—	—	—
		+0.298 σ	+0.295 σ	+0.299 σ	—	—	—
		-0.335 ^a					

† Underlined values represent the first ionisation potential of the molecule; ^a Brolsford *et al* (1960); ^b Morrison and Nicholson (1952); ** Misra (1970), semi-empirical molecular orbital calculations on some substituted benzenes; *** Yadav (1973), molecular orbital study of electronic structure, spectra and excited state geometry of some substituted benzenes.

3.3 Net atomic charges

The net atomic charges at various atomic sites are presented in figure 1. The conclusions drawn from these calculations are:

1. We observe that qualitatively the results obtained by 4-31G, 6-31G and 6-31G* methods are similar but quantitatively the magnitude of the net charges on each atomic site of the carbon in the 4-31G and 6-31G methods is less than in the 6-31G* method whereas this order is reversed for the substituent fluorine. However, the magnitude of the net charges on the hydrogen atoms attains approximately the same value in all the methods.
2. A very interesting aspect of these results is that the hydrogen atoms, which in π -electron approximations were not considered and carry only a small amount of

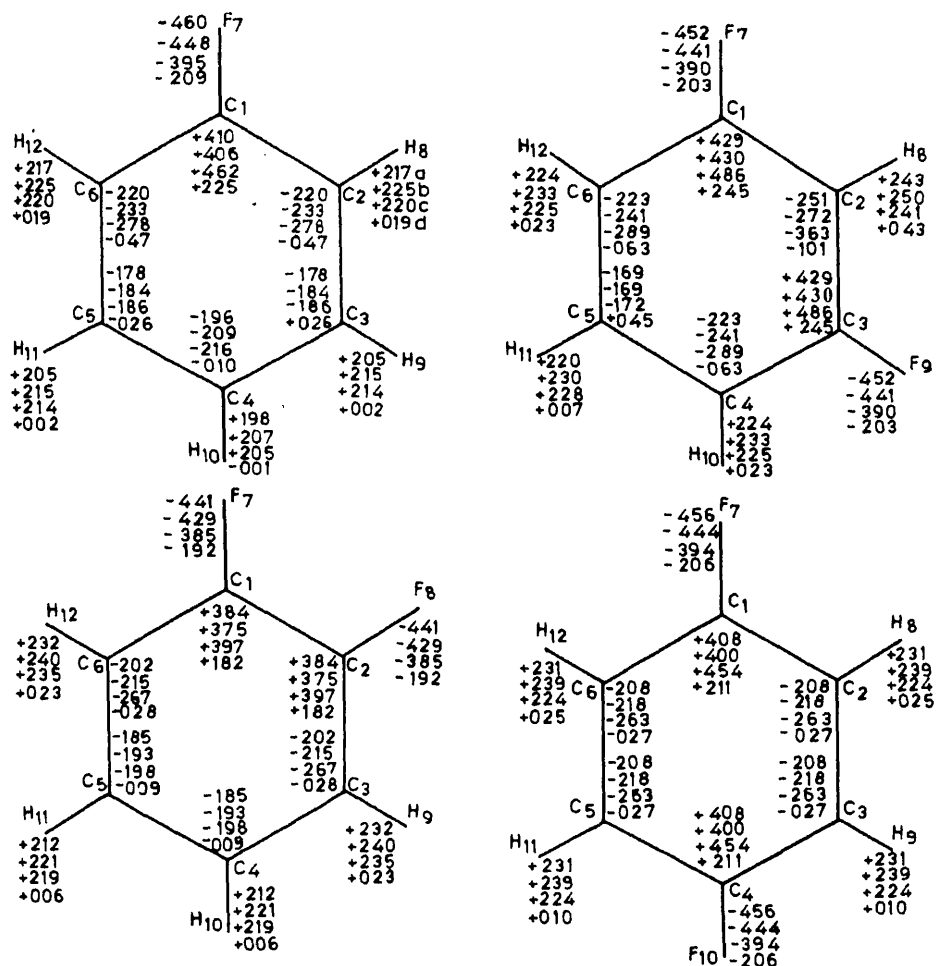


Figure 1. Net atomic charges in units of 10^{-3} electrons: (a) 4-31G (b) 6-31G (c) 6-31G* (d) CNDO/2 electron distributions (the values shown by the side of each atom refer to those

ve and -ve charges in semi-empirical all valence electron scf calculations (Yadav *et al* 1972a), tend to acquire very high values of only the positive charge indicating migration of electronic charge from hydrogen atoms to the ring.

We observe that whereas the substituent fluorine carries a net positive charge in π -electron calculations, they are negatively charged in our semi-empirical studies and the present study. This is because where π -electrons migrate from the fluorine to the ring making the former deficient in π -electrons, there is a large migration of the σ -electrons resulting in a net acquisition of negative charge by the fluorine. The fact that the fluorine carries a net negative charge and the hydrogen also has a net charge is not consistent with π -electron theories.

The semi-empirical all valence electrons calculations (Yadav *et al* 1973a) and even π -electron calculations carried out in the variable electronegativity formalism (Misra and Rai 1970, 1972), lead to some activation of the *m*-position in monofluorobenzene, but in the *ab initio* calculations no similar activation is obtained. However, if we disregard the charges migrating from the hydrogen to the carbon at the *m*-position, the *m*-position does get a small negative charge. It is also observed that the *o*-, *p*-, and *m*-directing property of this fluorine atom is mainly associated with the π -electron cloud of the system. The σ -charges do not correlate well with this property.

A comparison of the net charges on the fluorine atoms shows that they are modified substantially in difluorobenzenes as compared to the monoderivative. The magnitude of the net charges on fluorine atoms increases from *ortho* to *para* but it is maximum in monofluorobenzene. This mutual interaction of the substituents is exhibited clearly in *ab initio* as well as semi-empirical CNDO/2 methods (figure 1).

Dipole moments

Calculated dipole moments have been presented in table 2 and compared with semi-empirical calculations and experimental values. The calculated dipole moments are very close compared to their experimental values, however, the trends are reasonably well reproduced. The dipole moment corresponding to the polarized basis set 6-31G* are almost the same as the CNDO/2 (table 2) method and are close to experimental values. Similar values of the dipole moments of monofluorobenzene and *m*-difluorobenzene (table 2) have also been calculated by Boggs *et al* (1982) using the 4-21G basis set for optimized geometries.

Table 2. Dipole moments (Debye).

Molecule	Present calculation			Experimental	Earlier calculation (semi-empirical)	
	4-31G	6-31G	6-31G*		CNDO/2 ^b	INDO ^b
Monofluorobenzene	2.32	2.32	1.81	1.66 ^a	1.76	1.85
Difluorobenzene	3.98	3.98	3.11	2.59 $\pm$ 0.02 ^c	3.06	3.22
Difluorobenzene	2.31	2.31	1.80	1.51 $\pm$ 0.02 ^c	1.74	1.81

The redistribution of charges at various atomic sites of the molecules have been calculated by exciting an electron from HOMO to LUMO. As it is clear from table 1 that HOMO and LUMO are of π -symmetry, the change in orbital populations as compared to its ground state will take place in π -orbitals only. The redistribution of charges in the π -orbitals has been presented in figure 2.

The examination of MFB in figure 2 suggests that the *meta* carbon which was positively charged in the ground state gets negatively charged after exciting an electron from HOMO to LUMO. Correspondingly, the *para* carbon loses a considerable amount of charge in this process making it positively charged. Also the carbon at the *ortho* position becomes more negatively charged as compared to its value in the ground state.

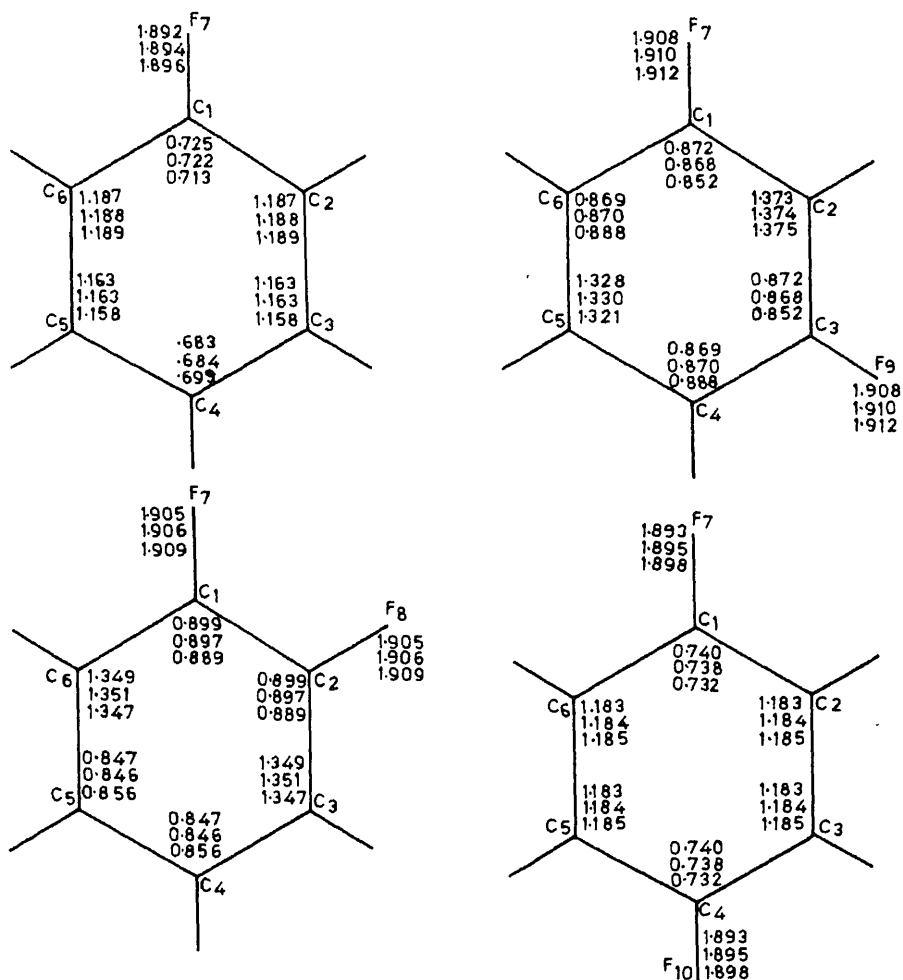


Figure 2. Redistribution of charges in the π orbitals at various atomic sites after exciting an electron from HOMO to LUMO (other orbitals are unaffected). The values by the side of each atom are obtained by the 4-31G (top), the 6-31G (middle) and the 6-31G* (bottom) methods.

However, the increase in the *ortho* position is less than that at the *meta* position. This *meta* directing features of fluorine in the excited state obtained by exciting an electron from HOMO to LUMO is found in all the three *ab initio* methods. Similar suggestions have been made (Del Bene and Jaffe 1968) on a large number of substituted benzenes using the CNDO/2 method. This suggests that certain reactions may proceed through excited states.

The π -orbital charges on the fluorine atoms and carbon atoms attached to the substituent in these molecules decrease from their ground state values. The difference between the two π -orbital charges on the fluorine and the carbon atoms attached to substituents are in the order *mono* > *para* > *ortho* > *meta*. The redistribution of the π -charge on the fluorine atom indicates that the π -electron donating capacity of the fluorine atom is more pronounced in such excitations and also that the carbon at the *meta* position in MFB is more populated.

4. Concluding remarks

The present study completes our MO calculations on mono- and difluorobenzenes. A detailed comparison of the results of different semi-empirical (both π -electrons and all valence electrons approximation) methods with the *ab initio* procedure suggests the same trend for the electronic properties of aromatic systems. However, the latter should be applied in order to explore the finer details of their chemical and spectroscopic properties.

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The willing and helpful co-operation by Prof. D K Rai is gratefully acknowledged. We are also thankful to Prof. S N Thakur and Dr B P Asthana for their stimulating discussions on the symmetry of orbitals. One of us (ops) wishes to thank Dr P P Singh, MLK College, Balrampur, and the UGC, New Delhi, for the award of a Fellowship.

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novel approach for the study of intermolecular interactions: molecular deformation densities

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Abstract. A new method to study intermolecular interactions via direct electron density measurements has been proposed. This approach involves the sum of constituent molecular electron densities as a reference rather than the usual sum of spherical atom densities for the evaluation of deformation densities. One may thus be able to focus specifically on the regions involving dominant intermolecular interactions such as hydrogen bonding, charge transfer, etc.

Keywords. Electron density; intermolecular interactions.

During the last two decades, reliable electron density measurements have become possible (Coppens 1982) due to development of x-ray instrumentation and better computational facilities. On the other hand, advances in quantum chemical methods have made it possible to theoretically compute these electron densities very accurately. The experimentalists normally report the maps of atomic deformation density (ADD) defined by

$$\Delta\rho(\mathbf{r}) = \rho_{\text{mol}}(\mathbf{r}) - \sum_{\text{Sph. atoms}} \rho(\mathbf{r}). \quad (1)$$

The spherical (sph.) atom densities in (1) are normally extracted from Hartree-Fock theoretical wavefunctions. These ADD do not highlight the accumulation of charge in the intermolecular regions since the major contributions to $\Delta\rho(\mathbf{r})$ as defined by (1) come exclusively in the proximity of the nuclei and from the bond regions. The intermolecular interactions are better monitored if the spherical atom concept is replaced by a constituent molecule or fragment formalism.

Let us consider two interacting molecules A and B and define the molecular deformation density (MDD) as

$$\Delta\rho(\mathbf{r}) = \rho_{\text{mol}}(\mathbf{r}) - \{\rho_A(\mathbf{r}) + \rho_B(\mathbf{r})\} \quad (2)$$

where, $\rho_{\text{mol}}(\mathbf{r})$ is obtained from an accurate x-ray diffraction experiment. The constituent molecular densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ can be obtained theoretically. These calculations can be carried out at various levels of accuracy by using standard software, say the set of GAUSSIAN programs. A good starting point for these computations could be at a 6-31 G level. A more elaborate DCI or higher-level CI calculation can also be taken up, if necessary. The geometries of the species A and B are to be frozen as they exist in the permolecule AB . In fact, the atomic co-ordinates in AB may be supplied by a high-order x-ray refinement from the above experimental data themselves. Thus the MDD

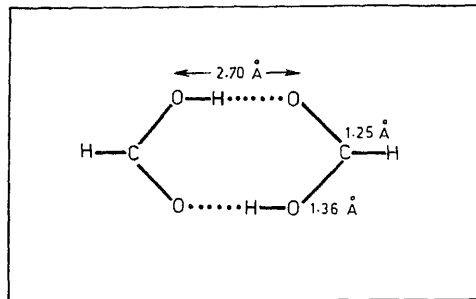


Figure 1.

defined via (2) are not marred by the features dominant around the atomic sites, but truly reflect the intermolecular interactions.

As an example, consider the classic case of the formic acid dimer (see figure 1). The experimental molecular electron densities for the dimer may be obtained by accurate x-ray diffraction studies (Coppens 1982). A calculation on the formic acid monomer in the dimer geometry (also obtained from the above experimental data) is then to be performed employing an extensive basis-set. The MDD's extracted thereby are expected to reveal the features of hydrogen bond in a more specific manner, i.e. they will not be wiped out by the otherwise dominant atom-centered functions. The molecular deformation densities would thus yield valuable information on hydrogen-bonded systems, charge-transfer complexes, etc. Exploratory studies outlined above, are currently being carried out on boric and formic acids.

An alternative approach based exclusively on the experimental data can also be developed. This involves the concept of molecular scattering factors in place of their atomic counterparts in the evaluation of monomer densities. However, a suitable shape function in terms of the centre of the mass of the molecule is needed to account for the thermal effects. It appears to us that this approach would be considerably more tedious than the one described earlier.

In conclusion, it is felt that a better approach for a systematic study of intermolecular interactions indeed needs to be developed. It is hoped that the above methodology based on molecular deformation densities provides one.

Acknowledgements

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Rapid Communications in Proceedings (Chemical Sciences)

From January 1985, the *Proceedings (Chemical Sciences)* publishes a new section devoted to rapid chemical communications. The objective of this section is to provide a medium for publication of novel and significant results in the different areas of chemistry which require rapid publication in order to establish priority and also to bring the work to the notice of the workers in the field without any delay. The length of such rapid communications should not exceed 4 printed pages.

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Investigations towards the synthesis of a CD-steroid intermediate

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Abstract. The development of a new synthesis of 2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a-methylindene was undertaken involving the preparation of 2,6,7,7a-tetrahydro-1 β -hydroxy-4-methoxymethyl-7a-methylindene because of the erratic yield in the last oxidation step of the reported synthesis of the former compound. Although various attempts to prepare the latter were not successful, interesting rearrangement products, the dienone, 5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione and the tricyclic keto alcohol, 2,6-diketo-3-methyltricyclo(5,2,1,0)decan-8-ol, were obtained, the structures of which have been proved by spectral data. Mechanisms for the formation of these products have been proposed.

Keywords. Methylindene; synthesis; spectral data; dienone; tricyclic keto alcohol.

1. Introduction

In the synthesis of 2,6,7,7a-tetrahydro-1 β -hydroxy-4-formyl-7a-methylindene (**1a**) (Banerjee *et al* 1976) and its optically active form (Banerjee *et al* 1983), considered to be an important synthon for the total synthesis of steroids, inconsistent yields were encountered in the last step involving oxidation of **1b** to **1a** by selenium dioxide. This prompted us to undertake the preparation of the methoxy compound (**1d**) that might be converted to **1a** via the hydroxy compound (**1c**).

2. Results and discussion

For this purpose, the methoxyaminoketone (**2a**), the diaminoketone (**2d**) and the ethoxyaminoketone (**2b**) were prepared, as described below, and subjected to the annelation reaction with 2-methylcyclopentan-1,3-dione (**5**) under various conditions.

For the preparation of the first compound, 2-methoxyethyl bromide (Tallman 1934) was added to sodium acetylide, prepared by bubbling dry acetylene through sodamide in liquid ammonia, to get 4-methoxybut-1-yne (**3**) in 66% yield. Mannich reaction with the compound (**3**), formaldehyde and diethylamine gave the methoxydiethylamine (**4**), which was hydrated with mercuric sulphate and aq. H₂SO₄ to give the methoxyaminoketone (**2a**) in 25% yield. The structural assignment was supported by spectral data. The regioselectivity in the hydration reaction was presumably due to the following reasons. In the acetylenic amine (**4**), the C-3 is electron-deficient because of the relatively stronger inductive effect of the nitrogen of the aminomethylene compared to that of the oxygen of the methoxymethylene, the latter being separated by one extra

methylene from the triple bond, and thus is open to attack by the nucleophilic h ion, leading to the formation of the ketone (2a). The structure of the aminoketone was further confirmed by its preparation by the following unambiguous procedure which incidentally proved to be a much better method because of the higher yield. The chloromethoxyketone (2e), obtained by the interaction of ethylene with β -methoxypropionylchloride in the presence of anhydrous $AlCl_3$, was treated with diethylamine in benzene to afford the aminoketone (2a) in 56% overall yield.

Various attempts, such as the Grignard reactions of 2-methoxyethylmagnesium bromide and vinylmagnesium bromide with 3-(diethylamino)-propionitrile and 3-methoxypropionitrile respectively gave back the starting compounds. The diethylamine reaction of the chloromethoxyketone (2f) (Jones and Taylor 1961) also failed to react with methanol, but with diethylamine the required chloroaminoketone (2c) was obtained as the minor product along with the second compound, the diaminoketone (2d) in larger quantity.

The third compound, the ethoxyaminoketone (2b) was prepared by the interaction of β -ethoxypropionylchloride and ethylene in the presence of anhydrous $AlCl_3$, followed by the chloroethoxyketone (2g) followed by its treatment with diethylamine in benzene.

The annelation reaction between the aminoketone (2a) and the dione (5) in the presence of pyridine followed by treatment with PTS (*p*-toluene sulphonic acid) gave the dienone (6) and the tricyclic keto-alcohol (7) (Danishefsky and Migdalof 1966). The structure of the dienone (6) was confirmed by its spectral data and by its conversion to the known compound (8) (Banerjee *et al* 1976) by catalytic hydrogenation.

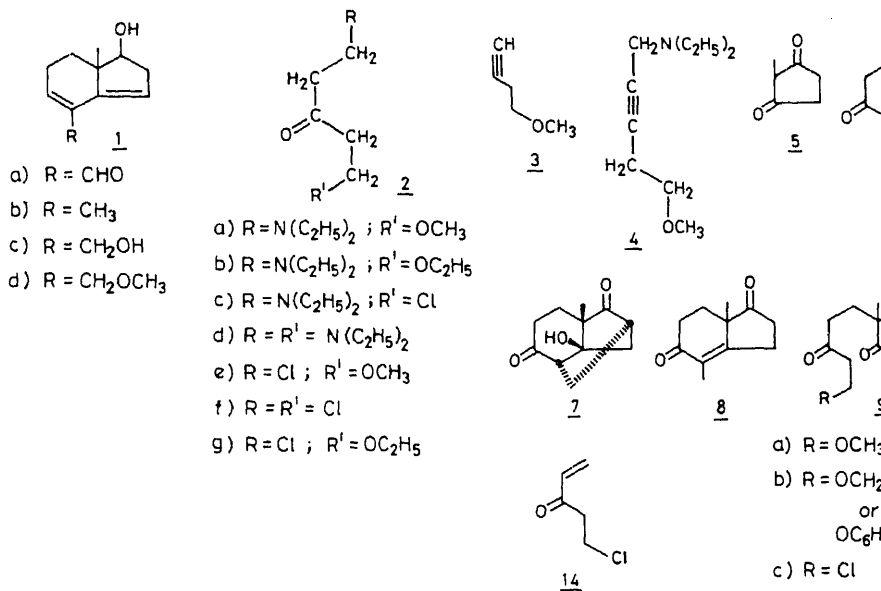
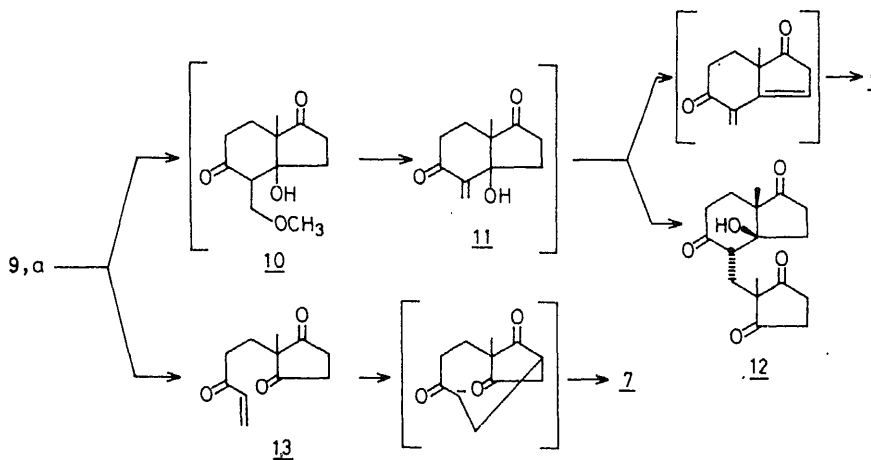


Chart 1.

The formation of the dienone (6) and the tricyclic keto alcohol (7) has been rationalised as follows (scheme 1). In the first case, the preliminary formation of the dienone (6) is followed by the formation of the tricyclic keto alcohol (7) by the reaction of the dienone (6) with the dione (5).

dehydration was proved by trapping the intermediate (11) in the reaction of triketone (9a) with one mole of the dione (5) in pyridine and benzene to give hydroxy tetraketone (12)*. In the second case, it is presumed that the triketone (9a) undergoes demethoxylation to give the intermediate unsaturated triketone (13) which is converted to the tricyclic keto alcohol (7)* according to the mechanism, proposed by Danishefsky (Danishefsky and Migdalof 1969a), who had prepared the compound (13) by the condensation of the chlorovinyl ketone (14) and methyl cyclopentane dione (5). It may be mentioned that while the addition of the dione (5) to the intermediate (11) to give the hydroxytetraketone (12) is facile, similar addition to the intermediate (13) is not favoured because of the obvious preference to that of the Danishefsky pathway mentioned earlier.



Scheme 1.

In the above mechanisms, the formation of the triketone (9a) has been assumed, actual formation of which was realized when the condensation was carried out under milder conditions, viz, the treatment of the aminoketone (2a) with the dione (5) in pyridine in benzene at room temperature. Attempts to prepare the triketones (9a and 9b) by the individual addition of methanol, benzylalcohol and phenol to the mixture of the chlorotriketone (9c) and vinyl triketone (13) (Danishefsky and Migdalof 1969) were futile.

Reactions with the diaminoketone (2d) or with the ethoxyaminoketone (2b) or with the triketone (9a) in place of 2a also resulted in the formation of the dienone (6) and the tricyclic keto alcohol (7).

3. Experimental

All boiling points and melting points are uncorrected. Anhydrous sodium sulphate has been used as the drying agent. The analytical data for compounds of series (2) are as follows:

reported as they are very labile. UV and IR spectra were determined on Shimadzu-180 and Perkin-Elmer 781 spectrophotometers. ^1H -NMR spectra were taken on Varian T-60 spectrometer. Chemical shifts reported are in δ values (ppm) relative to TMS as internal standard. The ^{13}C -NMR spectra were measured on a Bruker WH-270 spectrometer at 67.89 MHz in the pulsed mode. Mass spectra were determined on Atlas CH-4 spectrometer (70 eV).

3.1 4-Methoxybut-1-yne (3)

The acetylenic compound (3) was prepared by modifying a reported procedure (McCusker and Kroeger 1937). Sodium (9 g) was added in small portions to distilled liquid ammonia (≈ 550 ml), dry acetylene was then bubbled through it until a white suspension of sodium acetylide was formed. To this stirred suspension, 2-methoxyethylbromide (48 g) was slowly added dropwise and the stirring was continued for two hours with a stream of acetylene bubbling through the mixture. The ammonia was allowed to evaporate and a saturated solution of ammonium chloride was carefully added. The solution was chilled in a bath of ice-salt mixture and neutralized with 6N HCl. The product was collected after distillation by heating the reaction mixture on the waterbath, dried and redistilled to afford 20 g (66%) of the compound (3); b.p. $74-76^\circ$ (reported $86-87^\circ$). IR (neat): $\nu_{\max}$ 3300, 2850, 2150 cm^{-1} . ^1H -NMR (CCl_4): 1.9 (t , $J = 2$ Hz, 1H, $\text{C}\equiv\text{CH}$), 2.40 (dt , $J = 2$ Hz, 7 Hz, 2H, $-\text{CH}_2-\text{C}\equiv\text{C}$), 3.35 (S , 3 H, $-\text{OCH}_3$) and 3.45 (t , $J = 7$ Hz, 2H, OCH_2).

3.2 *N*-diethylamino-5-methoxypent-2-yne (4)

A mixture of 4-methoxybut-1-yne (3, 40 g), diethylamine (52 ml), acetic acid (30 ml), formalin (60 ml, 35% solution), cuprous chloride (0.8 g) and water (40 ml) was stirred under N_2 for 60 hr. The mixture was basified ($\text{pH} > 13$) with aq. NaOH, saturated with ammonium sulphate and extracted with ethylacetate (3×50 ml). The extract was washed with brine, dried and the solvent removed. The product (50 g, 63%) was isolated by distillation, b.p. $135-40^\circ/60$ mm. ^1H -NMR (CCl_4): 1.0 (t , $J = 7$ Hz, 6H, $-\text{N}-\text{CH}_2-\text{CH}_3$), 2.4 (m , 6H, $-\text{N}-\text{CH}_2-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_2-\text{OCH}_3$), 3.3 (S , 5H, $-\text{OCH}_3$ and $=\text{C}-\text{CH}_2-\text{N}-$) and 3.35 (m , 2H, $-\text{CH}_2-\text{O}-$). (Found: C, 71.23; H, 11.40; N, 8.31. $\text{C}_{10}\text{H}_{19}\text{NO}$ requires: C, 70.96; H, 11.32; N, 8.28%.)

3.3 *N*-diethylamino-5-methoxypentan-3-one (2a)

3.3a Preparation: A mixture of the amine (4, 3.3 g), conc. H_2SO_4 (1.4 ml) and mercuric sulphate (0.25 g) in water (15 ml) was stirred under N_2 at RT for 15 hr. The mixture was basified ($\text{pH} > 13$) with aq. NaOH and extracted with ethylacetate after saturation with ammonium sulphate. The extract was washed with brine and then dried, the solvent removed and the product isolated by column chromatography (neutral alumina, ethylacetate-hexane, 3:1); yield, 930 mg (25%); b.p. $61-64^\circ/50$ mm; IR (neat): $\nu_{\max}$ 1705 cm^{-1} ; ^1H -NMR (CDCl_3): 1.0 [t , $J = 7$ Hz, 6H, $-\text{N}(\text{CH}_2\text{CH}_3)_2$], 2.52 [m , 10H, $-\text{CH}_2-\text{N}(\text{CH}_2\text{CH}_3)_2$ and $-\text{CH}_2-\text{CO}-\text{CH}_2-$], 3.28 (S , 3H, OCH_3) and 3.64 (t , $J = 7$ Hz, 2H, OCH_2); Mass: M^+ m/e 187, m/e 86 (100%).

3.3b Improved method: To a stirred ice cold mixture of diethylamine (1.46 g) in

been described below, was added dropwise and left for 4 hr at 0°. The reaction mixture was basified (pH > 13) with dil. NaOH and extracted with ethylacetate. After removal of the solvent, the crude compound was distilled to get aminomethoxyketone (2a; 1.81 %); b.p. 61–64°/50 mm.

1-Chloro-5-methoxypentan-3-one(2e) and di-2-chloroethylketone (2f): To anhydrous AlCl₃ (67 g), dissolved in dichloromethane (250 ml) and cooled to 0°, was added dropwise β -methoxypropionylchloride (56 g). Ethylene was bubbled through the mixture for 4–5 hr, the temperature being maintained between 0 and 5°. The reaction mixture was poured into crushed ice containing 100 ml of conc. HCl and extracted with dichloromethane. The organic layer was washed successively with water, NaHCO₃ solution, water, brine and then dried. After removal of the solvent under reduced pressure, the crude compound was chromatographed over neutral alumina. The first fraction (hexane-benzene, 1:1) gave di-2-chloroethylketone (2f; 5.6 g) which was identified by comparison with an authentic sample (Jones and Taylor 1961), and the second fraction (hexane-chloroform, 1:3) gave the required methoxychloroketone (2e; 34.8 g, 68 %); b.p. 131–135°/5 mm; IR (neat): $\nu_{\max}$ 1720 cm⁻¹; ¹H-NMR (CCl₄): 2.66 (t, J = 7 Hz, COCH₂CH₂O-), 2.93 (t, J = 6 Hz, 2H, COCH₂CH₂Cl), 3.33 (s, 3H, OCH₃), 3.53–3.8 (m, 4H, -CH₂O- and -CH₂Cl).

3.3c Attempted preparation of the aminoketone (2a) by a two-step conversion of dichloroketone (2f)—1-Chloro-5-(diethylamino)pentan-3-one(2c) and di-2-(diethylamino) ethylketone(2d): A mixture of dichloroketone (2f; 1.55 g), diethylamine (1.4 g) and benzene (25 ml) was stirred at 0° for 4 hr. The reaction mixture was basified with dil NaOH and extracted with benzene. After the removal of the solvent, the crude compound was chromatographed over neutral alumina. Elution with hexane-chloroform (1:1) gave the starting dichloroketone (0.79 g), elution with chloroform initially afforded the monoaminoketone (2c; 0.17 g, 9.1 %) and then the diaminoketone (2d; 0.53 g, 23 %), as the last fraction; IR (neat): $\nu_{\max}$ 1710 cm⁻¹; ¹H-NMR (CCl₄): 1.9–2.1 (m, 12H, methyl H), 2.32–2.76 (m, 16H, methylene H).

As the required monoaminoketone (2c) was obtained in very poor yield, the second step, i.e. treatment with methanol was not carried out.

3.4 N-diethylamino-5-ethoxypentan-3-one (2b)

β -Ethoxypropionylchloride was treated with ethylene in the presence of anhydrous AlCl₃ to get the chloroethoxyketone (2g; 53 %; IR (neat): $\nu_{\max}$ 1715 cm⁻¹) which on treatment with diethylamine in benzene afforded (2b in 65 % yield. IR (neat): 1710 cm⁻¹; ¹H-NMR (CDCl₃): 0.91–1.25 (m, 9H, -N(CH₂CH₃)₂ and -OCH₂CH₃), 2.28–2.60 (m, 10H, -CH₂-N(CH₂CH₃)₂ and -CH₂COCH₂) and 3.23–3.58 (m, -CH₂-OCH₂CH₃).

3.5 5,6,7,7a-Tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione(6) and 2,6-dike-

which was then refluxed with a Dean-Stark attachment. After 4 hr, the solution was thoroughly washed with water, concentrated under vacuum and chromatographed over silica gel. Elution with chloroform initially gave 5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione (6, 0.71 g, 59 %) as the major product, which was further purified by a shortpath distillation; 136–140°/2 mm. UV (C_2H_5OH): λ_{max} 290 and 300 nm (ϵ 9300 and 11 000); IR (neat): ν_{max} 1710 and 1670 cm^{-1} ; 1H -NMR (CCl_4): 1.28 (s, 3H, CH_3), 1.88 (s, 3H, olefinic CH_3), 1.60–2.82 (m, 4H, $-CH_2-$), 6.32 (d, $J = 3$ Hz, 1H, olefinic α -H) and 7.06 (d, $J = 3$ Hz, 1H, olefinic β -H); Mass: M^+ m/e 176, m/e 161, m/e 133. (Found: C, 74.91; H, 6.90; $C_{11}H_{12}O_2$ requires C, 74.97; H, 6.86 %.)

Its structure was further confirmed by its conversion to the known compound (8) by the following procedure.

An ethanolic solution of the dienone (6, 260 mg) was hydrogenated over 5 % Pd-C catalyst (30 mg) for four hr when a little more than one equivalent of hydrogen was absorbed. The catalyst was filtered, the solution concentrated under vacuum and chromatographed over silica gel (hexane-ethylacetate, 1:1) when the compound (8) was obtained as a gummy material. The structure was confirmed by the direct comparison of the spectral data and by TLC with those of an authentic sample (Banerjee *et al* 1976).

Further elution with chloroform furnished the white crystalline compound (7, 0.12 g, 12 %), which was recrystallized from hexane-benzene; m.p. 170–171° (reported 172–174°, Danishefsky and Migdalof 1969a), IR (nujol): ν_{max} 3360, 1735 and 1690 cm^{-1} ; 1H -NMR ($CDCl_3$): 1.13 (s, 3H, CH_3), 1.62–2.66 (m, 10H, methylenes and methine protons), 4.9 (s, 1H, OH, exchangeable with D_2O); Mass: M^+ m/e 194 and m/e 69 (base peak).

3.6 2-(5-Methoxy-3-ketopentyl)-2-methylcyclopentan-1,3-dione (9a)

3.6a Preparation: A mixture of the aminoketone (2a; 1.9 g), 2-methylcyclopentane-1,3-dione (5, 1.1 g), dry benzene (20 ml) and pyridine (2.5 ml) was stirred at RT for 24 hr. The solution was cooled, diluted with benzene, washed successively with dil. HCl, water, aq. $NaHCO_3$ and water and then dried. The solvent was removed under vacuum and the residue on distillation gave the pure methoxytriketone (9a; 1.54 g, 65 %); b.p. 176–183° (≈ 1 mm). IR (neat): ν_{max} 1750, 1710, 1705 and 1110 cm^{-1} ; 1H -NMR ($CDCl_3$): 1.11 (s, 3H, CH_3), 1.92 (t, $J = 7$ Hz, 2H, $-\underline{CH}_2-C-CH_3$), 2.50 (t, $J = 7$ Hz, 2H, $-\underline{CH}_2-CH_2-C-CH_3$), 2.63 (t, $J = 6$ Hz, 2H, $OCH_2-\underline{CH}_2-$), 2.81 (s, 2H, ring methylene), 2.83 (s, 2H, ring methylene), 3.32 (s, 3H, OCH_3) and 2.62 (t, $J = 6$ Hz, 2H, $-OCH_2-$); ^{13}C -NMR ($CDCl_3$): 18.66 (q, CH_3), 27.77 (t, $\underline{CH}_2-C-CH_3$), 34.73 (t, ring methylenes), 37.07 (t, $-\underline{CH}_2-CH_2-C-CH_3$), 42.72 (t, $-OCH_2-\underline{CH}_2-$), 55.08 (s, $C-CH_3$), 58.66 (q, OCH_3), 67.30 (t, $-OCH_2$), 208.16 (s, acyclic CO) and 215.77 (s, ring CO); Mass: M^+ m/e 266, m/e 211, m/e 125. (Found: C, 63.58; H, 8.00. $C_{12}H_{18}O_4$ requires C, 63.70; H, 8.02 %.)

3.6b Attempted preparation of alkoxytriketones (9a and 9b) by another method. Reaction between the mixture of chlorotriketone (9c) and vinyl triketone (13) and different hydroxy compounds: The mixture of triketones (9c and 13), prepared as per Danishefsky and Migdalof (1969b), except that DMSO was used as the solvent in place of monoglyme, was treated individually with one equivalent of the potassium salts of methanol, benzylalcohol and phenol in *t*-butanol at RT for 12 hr. The reaction mixtures

removal of the solvent the mixture of the unreacted triketones (9c and 13) and the hydroxy compounds (methanol, benzylalcohol and phenol) were obtained without a trace of any of the expected alkoxy triketones.

3.7 3a,4,5,6,7,7a-Hexahydro-3a-hydroxy-4-(1',3'-diketo-2'-methylcyclopentano-2'-methylene)-7a-methylindene-1,5-dione (12)

A mixture of the methoxytriketone (9a; 0.57 g), the dione (5, 0.28 g), pyridine (0.6 ml) and dry benzene (10 ml) was stirred at RT for 12 hr. The reaction mixture was diluted with benzene and washed successively with dil. HCl, water, aq. NaHCO₃ and water and dried. After removal of the solvent, the crude solid was crystallized from ethanol-hexane to give the pure compound (12, 0.61 g, 74 %; m.p. 192–4°); IR (nujol): $\nu_{\max}$ 3405, 1740, 1730 and 1710 cm⁻¹; ¹H-NMR (DMSO-d₆): 0.94 [s, 3H, COC(CH₃)CH-OH], 1.06 [s, 3H, CO-C(CH₃)CO], 1.32–2.78 (m, 15H, methylenes and methine protons) and 6.80 (s, 1H, OH, exchanges with D₂O); ¹³C-NMR (DMSO-d₆): 11.84 [q, -C(CH₃)-C-OH], 20.68 [q, CO-C(CH₃)-CO], 23.07 (t, -CH₂-CH₂-C-CH₃), 25.72 (t, -CH-CH₂-), 29.92 (t, HO-C-CH₂-), 32.64 (t, -CH₂-CH₂-C-CH₃), 34.54 (t, HO-C-CH₂-CH₂-), 36.15 (t, CO-CH₂-CH₂CO), 36.69 (t, COCH₂CH₂CO), 48.26 (d, CO-CH-), 52.12 [s, HO-C-C(CH₃)-CO], 53.54 [s, CO-C(CH₃)-CO], 86.02 (s, -C-OH), 207.01 [s, CO-C(CH₃)-CO], 217.78 (s, -CH₂-CO-CH) and 218.10 [s, CO-C(CH₃)-C-OH]; Mass: M⁺ m/e 306 (100 %), m/e 288, m/e 260, m/e 194, m/e 181, m/e 125 and m/e 112. (Found: C, 66.7; H, 7.21. C₁₇H₂₂O₅ requires C, 66.65; H, 7.24 %.)

3.8 Reactions of (i) di-2-(diethylamino)ethylketone (2d), (ii) N-diethylamino-5-ethoxypentan-3-one (2b) and (iii) 2-(5-methoxy-3-ketopentyl)-2-methylcyclopentan-1,3-dione (9a) with the view to prepare the expected enedione (1d)

(i) A solution of diaminoketone (2d; 0.23 g), the dione (5, 0.11 g), pyridine (0.23 ml) and xylene (20 ml) was refluxed for 16 hr. After the usual work-up, the crude compound was chromatographed over silica gel (hexane-chloroform, 1:1) when the dienone (6, 0.13 g, 77 %) was obtained, b.p. 138°/2 mm.

(ii) A mixture of ethoxyaminoketone (2b; 1.5 g), the dione (5, 0.9 g), pyridine (1.75 ml) and xylene (10 ml) was refluxed for 20 hr. After the usual work-up, PTS (1.0 g) to the xylene solution was added and the mixture was heated under reflux for 4 hr. After work-up and purification by column chromatography (chloroform), the dienone (6, 0.62 g, 49 %) and the tricyclic ketoalcohol (7, 0.31 g, 22 %) were obtained.

(iii) Treatment of the triketone (9a) with (a) pyridine in xylene, (b) pyridine in xylene followed by PTS and (c) pyridine in benzene gave different mixtures of the dienone (6) and tricyclic ketoalcohol (7), except that in the last case only the compound (6) was formed.

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Photochemistry of the carbon-halogen bond: some recent developments

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Abstract. The current status on the photochemistry of the carbon-halogen bond, incorporated in a wide variety of organic compounds, is presented. It mainly deals with the photolytic cleavage of the C-X bond in solution phase. The major development in this field has been the generation of saturated, vinyl and α -keto carbonium ions by photochemical methods. The factors that control the type of cleavage, viz, homolytic-heterolytic are discussed. The mechanistic aspects as well as the synthetic utility of the photoreactions of some organic halides are highlighted.

Keywords. Photoirradiation; homolytic cleavage; heterolytic cleavage; excited states; electron transfer.

Introduction

The photochemistry of organic halides has received extensive attention and quite a few review articles appeared on this topic during the period 1954-1973 (Steacie 1954; Major and Simmons 1964; Walling and Huyser 1963; Sammes 1973). In these studies, the common theme was the formation of radical products resulting from the homolytic cleavage of the carbon-halogen bond. However, in the mid-seventies, several research groups independently re-examined the photochemistry of various types of organic halides and it became evident that another competing primary photoprocess is the heterolytic cleavage of the carbon-halogen bond resulting in carbocation intermediates. This discovery not only helped to rationalize some of the seemingly anomalous previous results but also led to some novel synthetic applications. The aim of the present article is to highlight the recent developments in this field chiefly since 1975.

Alkyl halides

A major recent development in the photochemistry of alkyl halides is the demonstration for the first time of competing ionic and radical photobehaviour for a number of alkyl halides (Kropp *et al* 1976). These authors have shown that irradiation of alkyl bromides, and particularly iodides in solution is a convenient and powerful means for the generation of carbocations, especially of high energy. The synthetic utility of this method was shown by the generation of 1-bicyclo(2.2.1)heptyl cation which is not readily accessible by the conventional methods. Irradiation of

1-iodobicyclo(2·2·1)heptane 1 in methanol afforded principally the ether 3 ($Y = \text{OCH}_3$, 76%), accompanied by a small amount of the radical product, viz, bicyclo(2·2·1)heptane 2 (12%). Similar type of photobehaviour was also observed in the case of 1- and 2-adamantyl iodides 4 and 5 which furnished essentially solvolysis products 7 (95%) and 8 (91%) respectively along with a trace of the reduction product 6.

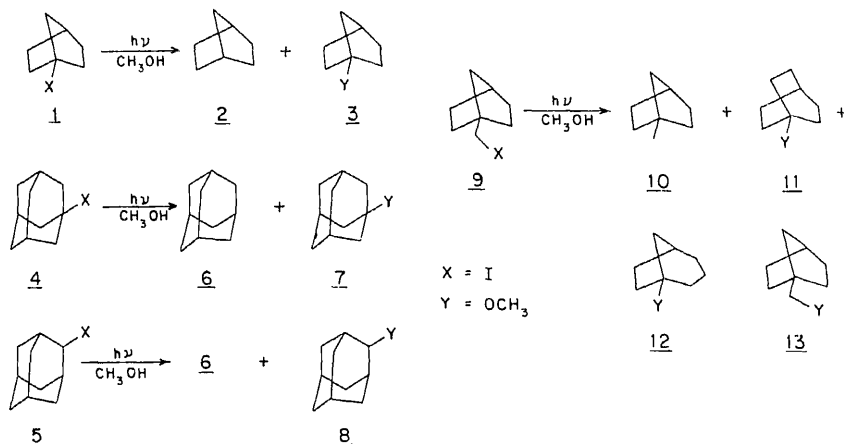
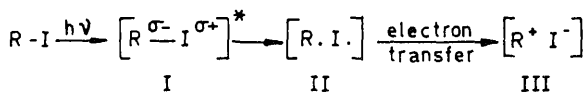


Chart 1.

Irradiation of iodide 9 in methanol, however, resulted in a mixture of the rearranged bicyclo(2·2·2) and bicyclo(3·2·1)octyl ethers 11 ($Y = \text{OCH}_3$, 37%) and 12 ($Y = \text{OCH}_3$, 47%). Significantly, the unrearranged ether 13 was found to be almost absent. Another interesting feature is that the iodide 9 displayed essentially an ionic photobehaviour as evidenced by the formation of the reduction product 10 only in trace amounts. This proclivity for rearrangement in the case of 9 has been ascribed to the involvement of 'free cations' (Keating and Skell 1970) generated by high energy processes with little or no solvent participation. The corresponding bromoanalogues displayed similar photobehaviour, although the radical products were preponderant.

The mechanism suggested by Kropp *et al* (1976) for the formation of cationic products is illustrated in scheme 1 for the alkyl iodide. It involves the photolytic generation of the radical pair II which can undergo an electron transfer to afford an ion pair III and ultimately the carbocationic products.

An essentially ionic photobehaviour has been observed for longibornyl iodide 14 and citronellyl iodide 18 (Gokhale *et al* 1976). The iodide 14 on irradiation in heptane



18 under similar conditions, furnished the simple elimination product 19 (52%) and yielded 20 (*cis* & *trans*, 42%) with π -participation alongwith minor amounts of 21 (6.0%). The formation of 16 is supposed to involve, 1,3-elimination while transannular shift is considered to be responsible for the generation of 17. An ionic pathway has been preferred to rationalize the photoproducts as the radical derived products were found to be almost absent.

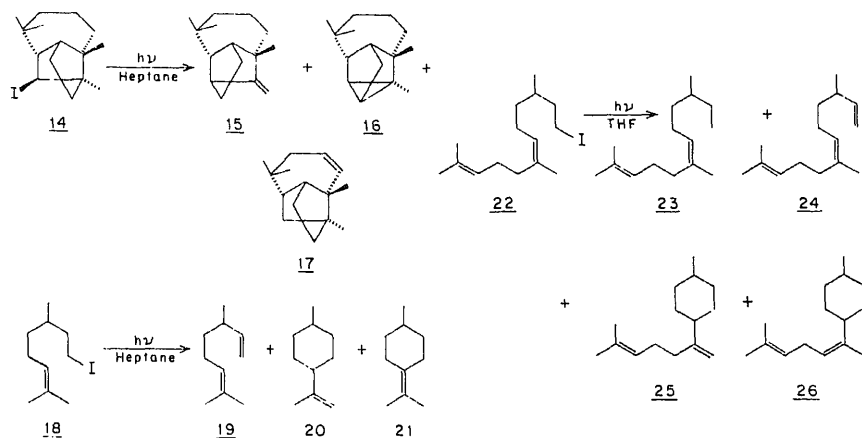


Chart 2.

Recently Saplay *et al* (1980) have extended their studies to systems of possible biomimetic interest and reported the formation of products arising from π -participation. These authors observed that photoirradiation of 2,3-dihydro-6(Z)-farnesyl iodide 22 in THF furnished 23 (5%), 24 (22%), 25 (40%) and 26 (21%) and three other minor unidentified products (12%). Similar irradiation of the corresponding *E*-isomer 27 afforded 28 (6%), 29 (35%), 25 (37%), 26 (18%) and two minor unidentified products (4%). The formation of these products has been rationalised using the concept of electron transfer.

Carbonium ions generated in a photolytic pathway appear to react differently from those formed in normal thermal reactions. For example, the primary 'free' cation generated by the photolysis of iodide 30 (Takaishi *et al* 1978) showed a preference for rearrangement yielding 31 while the same cation formed by the treatment of alcohol 32 with sulphuric acid afforded the hydrocarbon 33 by hydride abstraction.

A novel photobehaviour of isomeric chlorides present in the (2.2.1) and (2.2.2) bicyclic systems has been reported recently (Morrison and Miller 1980). Photolysis of a methanolic solution of *exo*-2-benzonorbornenyl chloride 34 with 254 nm light led to the cleavage of the C-Cl bond and furnished the products 35 (ϕ 0.12), 36 (ϕ 0.08), 37 (ϕ 0.03) arising from radical intermediates and the products 38 (ϕ 0.07), 39 (ϕ 0.13) and 40 (ϕ 0.03) involving the ionic intermediates. The formation of 40 is unique since it involves the hitherto unobserved 1,2-migration of the C₁-C₇ bridge in the 2-benzonorbornenyl cation. The generation of 'hot' carbocation by the aryl-initiated cleavage of the C-Cl bond has been suggested as being responsible for this rearrangement. The

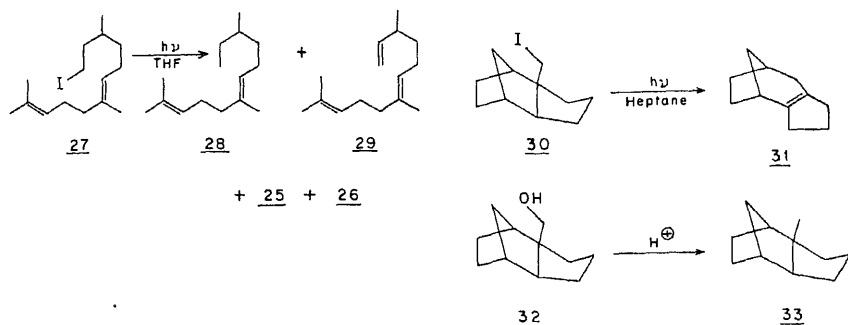
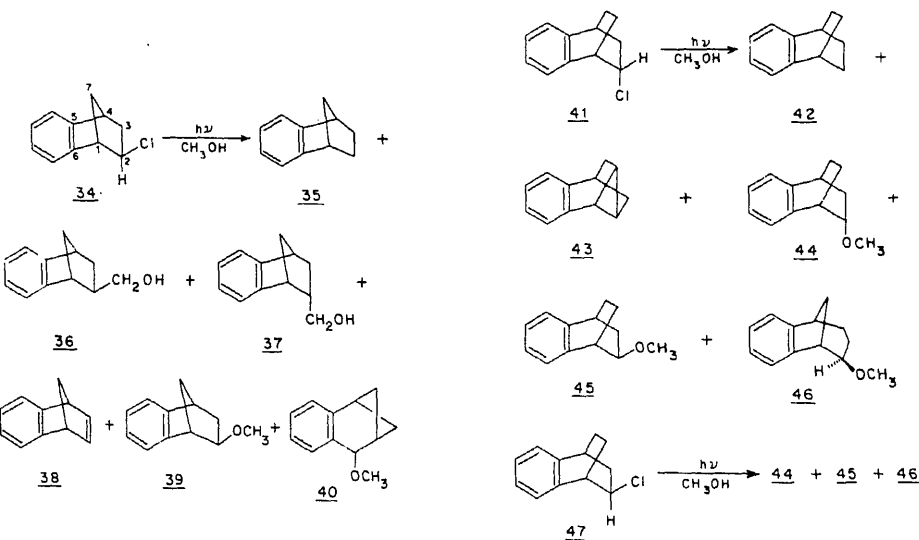


Chart 3.

corresponding *endo*-chloride, however, was found to be less (≈ 20 times) reactive than the *exo*-isomer 34. These products were shown to arise from the singlet excited state. The photolysis of isomeric chlorides in the bicyclo-(2·2·2)-octane system revealed an entirely opposite pattern of reactivity compared with that of the bicyclo-(2·2·1)-heptane system. For example, *endo*-2-chlorobenzo-bicyclo-(2·2·2)-octa-5-ene 41 was found to be more reactive (~ 5 times) than its *exo*-isomer 47 and on photolysis in methanol afforded the ionic products 43 (5%), 44 (37%), 45 (11%) and 46 (6%) together with some radical derived product 42 (22%). The rearranged ether 46 and the cyclopropane product 43 are supposed to have originated from a 'hot' carbocation. The product mixture from the photolysis of the *exo*-chloride 47 was less complex and comprised essentially the ionic products 44–46.



radical-derived as its yield was reduced when the irradiation was carried out in presence of oxygen. The iodide 50 under similar conditions of irradiation afforded the cationic products 51 (37%) and 52 (28%). Another study of the photochemistry of 48 in alcoholic solvents resulted mostly in ionic products comprising 49 (60%), 53 (23%) and 54 (7%). Similar irradiation of 56 offered the ionic product 57 exclusively, suggesting the possible involvement of the phenonium ion (Bhale Rao 1978).

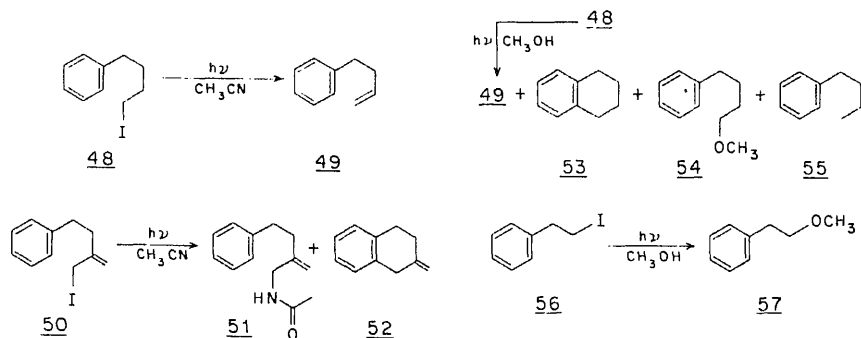
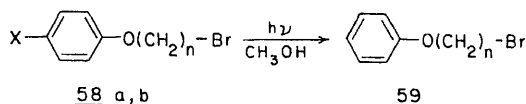


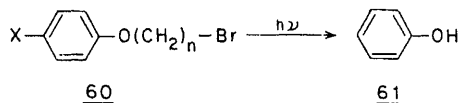
Chart 6.

The photochemistry of a number of ω -(4-halo phenoxy)-alkyl bromides 58 a, b have been studied in methanol (Davidson and Goodin 1980). These authors observed a selective cleavage of stronger aryl-halogen bonds (Ph-Cl = 94.5 kcal/mole, Ph-Br = 79.2 kcal/mole) rather than alkyl-bromine bonds ($\text{CH}_3\text{CH}_2\text{-Br}$ = 60 kcal/mole) to give 59 in all cases except for 58b with $n = 2$. The absence of the reaction of the alkyl-bromine bond has been attributed to the inefficient energy transfer from the aryloxy group to the $\text{CH}_2\text{-Br}$ bond.

It has been shown that intramolecular sensitized homolysis of alkyl-bromine bonds can occur efficiently in 60 with $n = 2$ and 3 only as these were found to be far more



a, X = Br; b, X = Cl;
 $n = 2, 3, 4, 6, 10$



X = H $n = 2$ 80 % ; $n = 3$ 65 %
 $n = 4$ 16 % ; $n = 6$ 8.0 %
 $n = 10$ no reaction

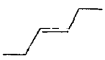
reactive in giving the phenol 61 than the corresponding higher homologues. In the above cases, aryl-halogen bond cleavage was shown to involve the first excited singlet state. Similar observations have been reported in the photochemistry of alkyl bromides and iodides incorporated in naphthyl ethers (Kessar *et al* 1980).

The photochemistry of diiodomethane has been elegantly utilized for the cyclopropanation of various types of olefins (Kropp *et al* 1981). This photolytic method appears to be significantly less subject to steric effects than the traditional Simmons-Smith method (Simmons *et al* 1973). The α -iodo cation, viz, ICH_2^+ is suggested as the methylene transfer species in the cyclopropanation. Representative examples of photocyclopropanation of a few alkenes are presented in scheme 2.

The photochemistry of some bridgehead iodides has been described recently (Kropp *et al* 1982). The iodides 62, 63 and 64 on irradiation in methanol afforded principally the ionic products 68 (90%), 69 (91%) and 70 (81%) accompanied by small amounts of reduction products 65 (2%), 66 (4%), and 67 (15%) respectively. It has been demonstrated that the ionic products 68–70 originate from the bridgehead carbocations and not by the protonation of bridgehead alkenes. By contrast, deuterium labelling studies revealed the intermediacy of the bridgehead alkene in the genesis of the ionic product 76 in the photolysis of 71 in methanol.

3. Allylic and benzylic halides

Cristol *et al* (1978) have reported the photochemistry of allylic halides incorporated in the dibenzobicyclic nonatriene and benzoctadienyl systems. The halide 79 on irradiation at 254 nm in aqueous CH_3CN was transformed into a mixture of 80, 81, 82 and 83. These products are considered to arise from photo-Wagner-Meerwein rearrangement and photochemical Ritter reaction. Irradiation of 79 in different solvents showed that the quantum efficiency decreased with the lowering of solvent polarity and the product composition also depended on the solvent polarity. Quenching experiments revealed that photosolvolysis products arise from the singlet

Alkene	Cyclopropane	Yield* (%)	Alkene	Cyclopropane	Yield* (%)
		68 (33)			76 (16)
		60 (47)			83 (42)
		75 (36)			30 (0)

* Numbers in parentheses are yields of Simmons - Smith method

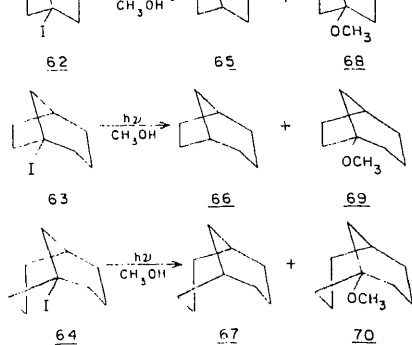


Chart 8.

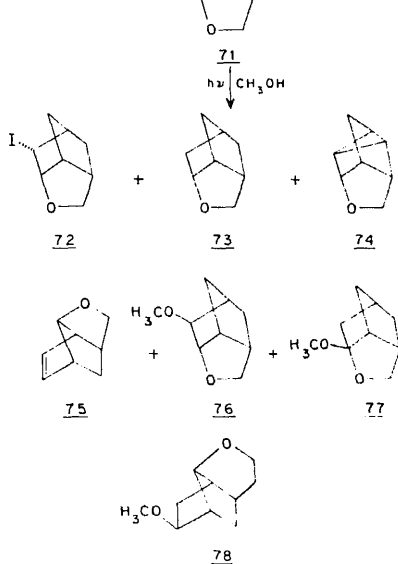


Chart 9.

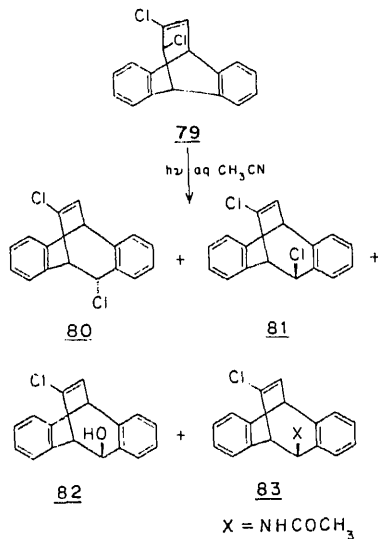
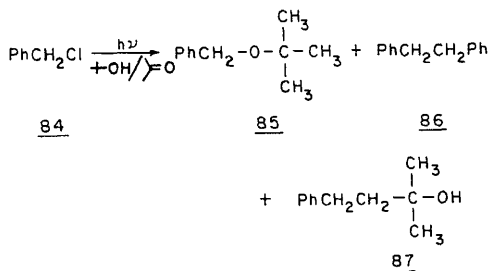


Chart 10.



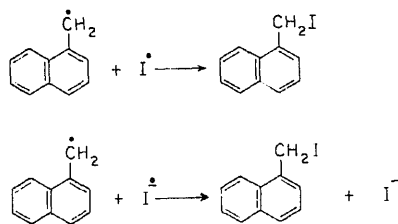
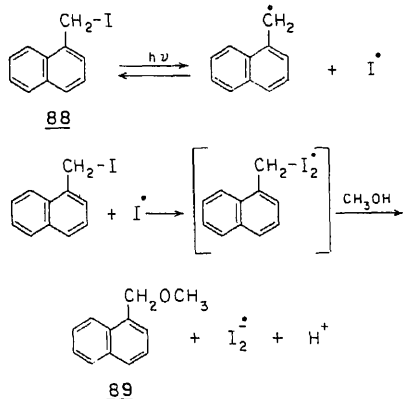
excited state. An analogous type of photobehaviour has been displayed by the halides derived from benzoctadienyl systems.

Recently, several research groups have studied the photochemistry of benzyl halides under a variety of conditions. Most of the work deals with the effects of direct irradiation, photosensitization and solvent variation upon quantum yields of photo-induced heterolysis and homolysis of the carbon-halogen bond. Appleton *et al* (1980) have examined the photochemistry of benzyl halides in methanol and *t*-butyl alcohol.

They report that the ionic products and the products derived from non-ionic mechanisms are formed in either direct or sensitized photolysis. The significant feature of the mechanism proposed by them is the interconversion of loose singlet and triplet radical pairs and electron transfer in the singlet pair to give a solvent separated ion pair.

A detailed investigation of the photochemistry of benzyl chloride 84 and a number of its *m*- and *p*-substituted derivatives in *t*-butyl alcohol has been carried out (Cristol and Bindel 1980). Both the types of products, viz, photosolvolysis product benzyl *t*-butyl ether 85 and photohomolysis products bibenzyl 86 and 4-phenyl-2-methyl-2-butanol 87 were observed in both direct and photosensitized irradiations. Furthermore, these authors have reported that bond heterolysis is favoured in sensitized conditions while direct irradiation favours homolytic cleavage. Cristol and Bindel (1981) in their study of the photochemistry of a number of substituted benzyl chlorides, have employed a variety of sensitization and quenching techniques. The results obtained are rationalized by the assumption that there are two triplet states of benzyl chlorides—one, a short-lived upper state which leads to solvolysis products and another, a long-lived lower energy state.

An altogether different mechanism has been proposed for the formation of the ether 89 in the photolysis of iodomethylnaphthalene 88 in methanol (Slocum *et al* 1981). The product generating step has been shown to involve a complex between the iodine atom and the starting halide. The complex thus formed, would rapidly dissociate into separate ions or react directly with the solvent (scheme 3).



4. Vinyl halides

The photochemistry of vinyl halides has received relatively less attention although these compounds could be potential sources of vinyl radicals and vinyl cations depending upon the mode of cleavage of the carbon-halogen bond. It must be pointed out that in most of the cases reported so far, photoreduction of the vinyl radicals occurs almost

1976). For example, irradiation of 90 for 2.5 hours in deuterated methanol gave deuterated olefin 91 (60 %). The high stereospecificity observed in this case is somewhat surprising especially with the involvement of vinyl radical intermediates. Irradiation of 92 under similar conditions gave 93 in a high yield (94 %).

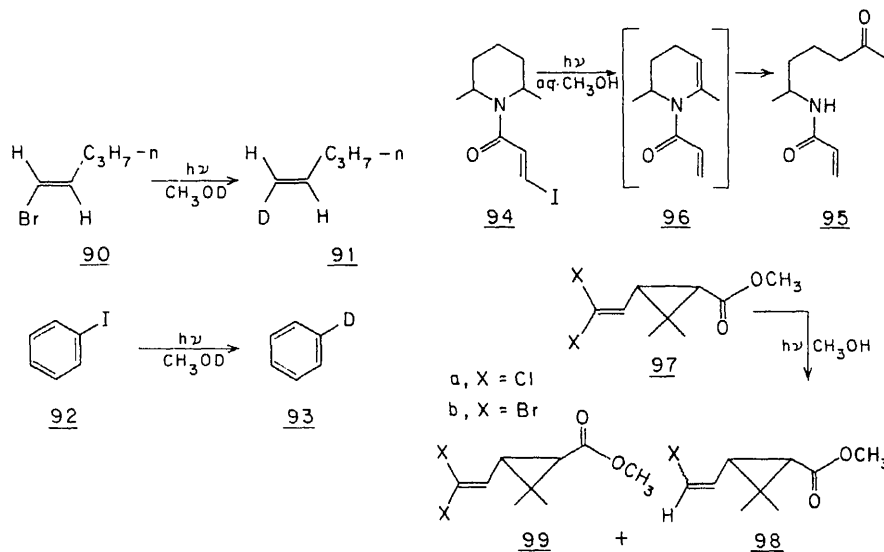


Chart 12.

A new method of remote functionalization involving the photoinduced cleavage of the carbon-halogen bond has been attempted in the case of various β -iodoacrylamides (Wilson and Commons 1975). For instance, irradiation of 94 in aq. methanol gave the keto-amide 95 (77 %) with a newly functionalized carbon. The probable mechanism suggested by the authors involves the abstraction of a hydrogen atom β - to the amide nitrogen by the vinyl radical leading to the enamide intermediate 96 which can rapidly hydrolyze to the final product.

The modern synthetic pyrethroids containing the haloethylenic moiety are known to possess enhanced insecticidal potency with higher photostability (Elliot and Jan 1978). The photoprocesses of this class of compounds include reductive dehalogenation and *cis-trans* isomerization at the cyclopropane ring. The compounds 97 a, b irradiation in methanol at 254 nm resulted mainly (Ruza and Casida 1979) in 98 a, b (92 %; b, 58 %) and 99 a, b (a, b: 8 % each). Sensitization and quenching studies show that the triplet excited state was responsible for the isomerization at the cyclopropane ring.

There are some recent reports which show that photolysis of certain vinyl halides is a particularly facile route to the corresponding vinyl cations. Suzuki *et al* (1976) have observed a novel photoinduced 1,2-anisyl migrations leading to the corresponding tolanes 101 a-c (a, 53 %; b, 86 %; c, 50 %) in the irradiation of 2,2-dianisyl vinyl bromide 100 a-c in benzene. By contrast, photolysis of 100d in benzene did not afford the corresponding tolanes but gave a mixture of 9-phenylphenanthrene 102 (40 %) and

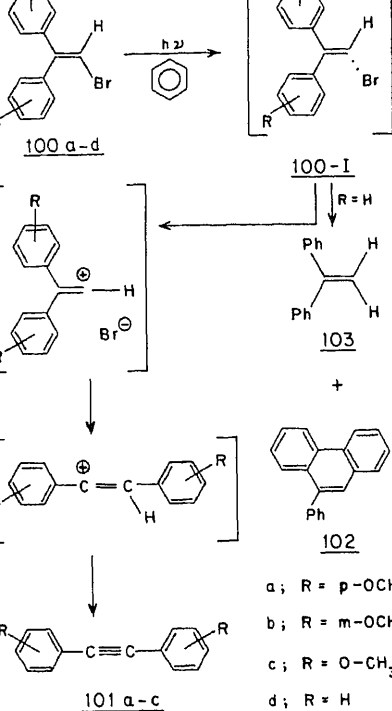


Chart 13.

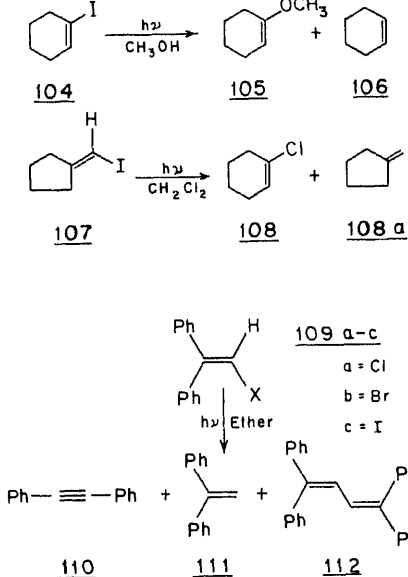


Chart 14.

1,1-diphenyl ethylene **103** (13%) as a result of radical reactions via the radical pair **100-I**. Simultaneously, McNeely and Kropp (1976) have observed that cycloalkenyl halides as well as halomethylene cycloalkanes on photoirradiation result in vinyl-cation derived products together with radical products. Irradiation of **104** in methanol furnished the ionic product **105** (65%) accompanied by the reduction product **106** (25%). Similar ionic behaviour was exhibited by **107** which gave the ring-expanded product **108** (23%) alongwith the radical product **108a** (50%). As mentioned earlier in the case of alkyl halides, these reactions have also been interpreted to involve electron transfer within the initially generated radical pair affording vinyl cations.

Recently, 1,1-diphenyl-2-haloethylenes **109 a-c** have been subjected to a detailed photochemical study in different solvents (Sket and Zupon 1979). Competing ionic and radical behaviour has been observed for these vinyl halides. Free radical intermediates were supposed to be involved in the formation of **111** (a, 28%; b, 34%; c, 51%) and **112** (a, 10%; b, 10%; c, 6%) while **110** (a, 25%; b, 23%; c, 19%) was ascribed to an ionic intermediate. The products were rationalized using the mechanism of electron transfer.

An example of nucleophilic trapping of a photolytically generated vinyl cation is provided by Kitamura *et al* (1979). These authors irradiated the vinyl bromide **113** in acetone in presence of tetrabutylammonium azide and obtained the oxazoline **116** (90%) as the final product. The vinyl cation was trapped by the azide ion and the

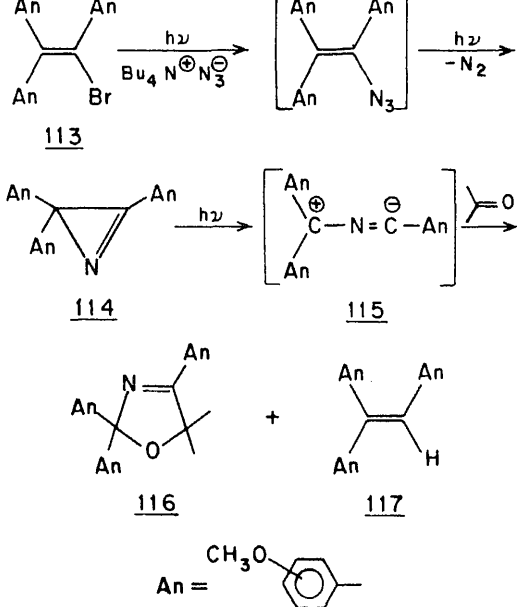


Chart 15.

resulting vinyl azide gave the azirine 114 by loss of nitrogen. On further photolysis, 114 gave the product 116 via the nitrile yield 115 by a cycloaddition reaction with acetone. The reduction product 117 was obtained in a poor yield (5%).

Direct evidence for vinyl cation intermediates in the case of vinyl halides has been obtained by ^{13}C NMR (Siehl *et al* 1974) as well as flash photolysis studies (Kitamura *et al* 1980). In the ^{13}C NMR spectrum of 1,1-dimethyl-2-(*p*-anisyl)-2-fluoroethylene when recorded in the presence of SbF_5 , the observed downfield shift (30 ppm) of the signal of the carbon carrying methoxyl group was considered as evidence for the vinyl cation at C_2 (Siehl *et al* 1974).

The photolysis of β,β -bis (*o*-methoxyphenyl)-substituted vinyl bromides 118 ($R = \text{H}, \text{CH}_3, \text{Ph}$) in benzene has been reported to give essentially the benzofurans 119 and 120 (Suzuki *et al* 1981). With α -aryl substituted systems, the benzofuran is derived essentially from the unrearranged vinyl cation 118I but when the α -substituent is methyl or hydrogen, benzofuran from the rearranged vinyl cation 118II is also formed. With the α -methyl substituent, the allene 121 (20%) was also observed.

A systematic investigation carried out on the photochemistry of vinyl halides derived from camphene revealed the occurrence of competing radical and ionic photoprocesses (Sonawane *et al* 1984a). The unsubstituted vinyl halides 122 and 123 on direct irradiation in methanol furnished exclusively the radical-derived product 124, while the halides 125 and 126 on similar irradiation afforded both the radical products, viz, *E/Z* isomers of ω -methyl camphene 127 (65%) and the ionic product 128 (35%). Similarly, ω -phenyl substituted halide 129 on direct irradiation resulted in the radical and ionic products 130 (24%) and 131 (76%) respectively. However, these vinyl halides when irradiated in nonpolar solvents such as cyclohexane and methylene chloride gave

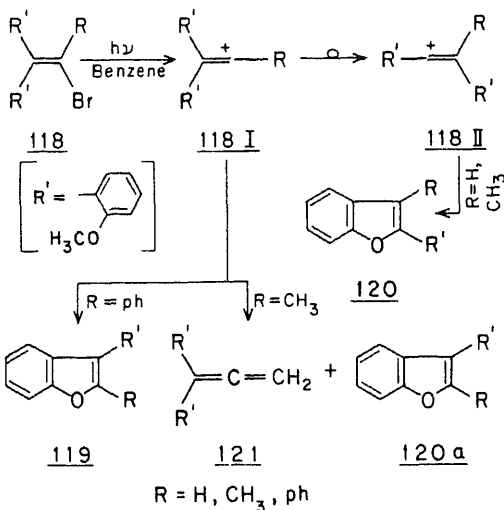
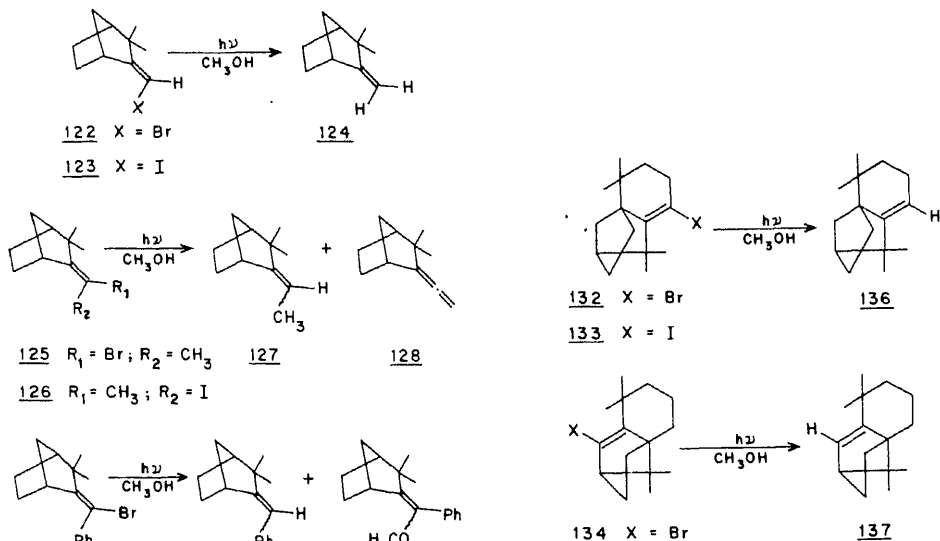


Chart 16.

radical and ionic photobehaviour of these vinyl halides is governed mainly by two factors, namely: (1) the nature of the α -stabilizing substituent, and (2) the polarity of the medium. The sensitization and quenching studies carried out with these substrates clearly established for the first time that the triplet excited state is responsible for the radical products while the ionic products are derived from the singlet excited state.

The results obtained from the irradiation of cyclohexenyl halides 132–135 are noteworthy (Sonawane *et al* 1984b). It is significant to note that these halides on irradiation in methanol yielded only the radical-derived reduction products 136 and 137, thereby confirming the earlier findings (Sonawane *et al* 1984a). In the light of these



results, the facile generation of vinyl cations in the photolysis of cycloalkenyl halides lacking α -stabilizing substituents (McNeely and Kropp 1976) appears somewhat surprising. It remains for future workers to rationalize these intriguing differences.

5. α -Halo ketones

The effect of the carbonyl moiety on the photochemistry of the carbon-halogen bond has been the subject of some recent studies. In this section, a few selected examples of the photobehaviour of this class of compounds are presented. Photolysis of 9-bromo-acetylanthracene 138 (Matsumoto *et al* 1974) in cyclohexane led to the discovery of two photochemical reactions of this class of compounds. The major photoproducts were 1-aceanthrone 140 and 9-bromo-anthracene 141. The intermediate 139 detected spectroscopically is supposed to give 140 either by thermal or photochemical process with loss of HBr. The product 141 is suggested to arise from a concerted process involving loss of ketene.

A similar type of photocyclization giving indane-1-one 143 (62%) occurs (Bergmark 1978) especially in the case of α -chloro-*o*-methyl-acetophenone 142 but not its bromoanalogue which gave only the reduction product 144. The cyclization product is supposed to involve photoenolization while 144 seems to be derived from an α -keto radical formed in the homolysis of the C-X bond. The fluorine substitution α to the carbonyl group as in 145 is found to cause a dramatic effect with the exclusive formation of 146 providing a unique method for the synthesis of fluorinated cyclobutanols (Wagner and Thomas 1976). The alteration in the Norrish-II product ratio caused by α -fluorine substitution is considered to be due to hyperconjugative stabilization of the 1,4-diradical. However, fluorine substitution at the γ -position does not influence the product ratio.

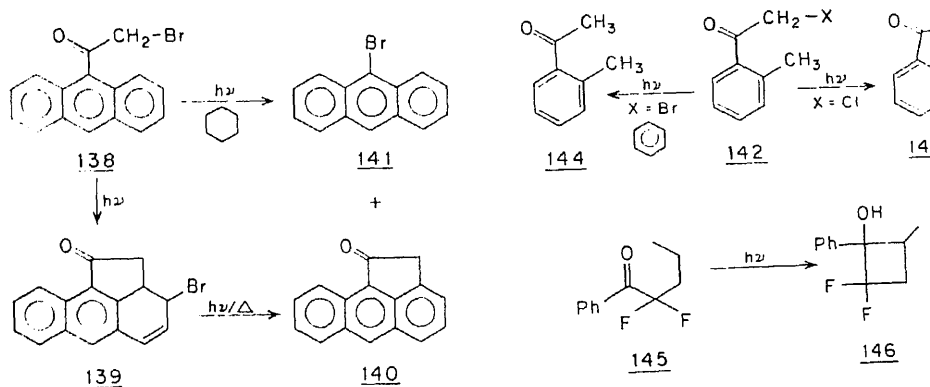


Chart 19.

152 into the intermediates 153 *a, b* (98 %, 1:2 of *a* and *b*) which on treatment with alkali furnish the acid 154, a highly useful compound in the synthesis of pyrethroids (Martin *et al* 1979).

The photochemistry of β,γ -unsaturated α -chloroketones 155–158 has been investigated by Givens and Strekowski (1975). The exo-chloroketone 155 furnished 159 (55%) while the irradiation of the endo-isomer 156 under similar conditions gave a complex product mixture. Photolysis of the endo- and exo-chloroketones 157 and 158 resulted in the same products 160–162 in different proportions (exo- 160, 60%; 161, 10%; 162, 30%; endo- 160, 34%; 161, 10%; 162 26%).

The photolysis of the steroidal α -bromoketone 163 in dioxane led to the radical and ionic products 164 and 165, respectively, in a 1:1 proportion (Huppi *et al* 1966).

A systematic study of the photochemistry of some α -halocycloalkanones 166 *a-d* carried out recently (Purohit and Sonawane 1981) revealed the occurrence of competing radical and ionic photobehaviour. Sensitization and quenching studies indicated that the radical products (167 *a-d* (*a*, 28%; *b*, 16%; *c*, 90%; *d*, 70%)) arise from the $n\pi^*$ triplet states whereas the ionic products (168 *a-d* (*a*, 13%; *b*, 26%; *c*, 10%; *d*, 30%)) originate from the $n\pi^*$ singlet excited states, thus providing, for the first time, experimental support to the Wagner model (Wagner 1976) for the cleavage of the C–X bond in α -haloketones.

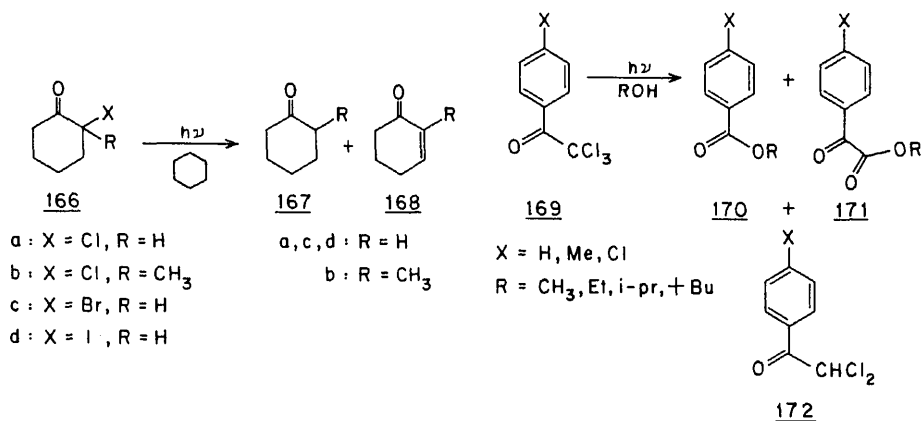


Chart 22.

Izawa *et al* (1980) have obtained the products 170 (23%), 171 (5%) and 172 (60%) from the photoinduced alcoholysis of substituted α,α,α -trichloroacetophenones 169. It is interesting to note that sensitization and quenching studies revealed that 170 and 171 arise from two different triplet excited states.

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Infrared and Raman spectra of three tetrametaphosphates $M_2P_4O_{12}$ ($M = \text{Fe, Ni, Zn}$)

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Abstract. The infrared and Raman spectra of three tetrametaphosphates $M_2P_4O_{12}$ ($M = \text{Fe, Ni, Zn}$) have been recorded and analysed. A factor group model has been used to interpret the spectra of $\text{Fe}_2P_4O_{12}$ and $\text{Ni}_2P_4O_{12}$. A free ion model could explain the $\text{Zn}_2P_4O_{12}$ spectra. The frequencies have been assigned on the basis of characteristic vibrations of PO_2^{2-} and P-O-P groups. The $\text{P}_4\text{O}_{12}^{4-}$ ion is found to have C_i symmetry in $\text{Fe}_2P_4O_{12}$ and $\text{Ni}_2P_4O_{12}$ and C_{2h} in $\text{Zn}_2P_4O_{12}$. The ion in $\text{Fe}_2P_4O_{12}$ is more distorted than in the other two.

Keywords. Vibrational spectra; tetrametaphosphates; free ion symmetry; P-O-P and PO_2^{2-} groups.

1. Introduction

The infrared and Raman spectra of certain tetrametaphosphates of monovalent and divalent metals (Polataev 1968; Tokman and Polataev 1976; Steger and Simon 1958), and double metaphosphates of alkali metals and rare earths (Maddi *et al* 1978; Xie *et al* 1982) have been reported. Most of their studies were in order to determine the possible symmetries of the anion ($\text{P}_4\text{O}_{12}^{4-}$) in those crystals. They explained the vibrational frequencies of the anion on the assumption that it contains the groups PO_2^{2-} and P-O-P. In these compounds the anion exists either as a chain or as a cyclic ring (Tokman and Polataev 1976; Maddi *et al* 1978; Palkina *et al* 1976). In the ring structure itself, different conformations are possible in different crystals (Polataev 1968).

Steger and Simon (1958a, b) reported a D_{2d} symmetry for the anion in $M_2P_4O_{12}$ ($M = \text{Mg, Cu}$) from IR studies. However, x-ray diffraction studies (Beucher and Gramer 1968; Bagieu-Beucher *et al* 1976) suggest a centre of symmetry for the anion in the crystals $M_2P_4O_{12}$ ($M = \text{Mg, Fe, Ni, Zn, Cu, Co, Mn}$). A detailed analysis of the vibrational spectra of these compounds is expected to give more information about the symmetry of the anion in these crystals. In the present paper the analysis of the IR and Raman spectra of the tetrametaphosphates $M_2P_4O_{12}$ ($M = \text{Fe, Ni, Zn}$) is reported.

2. Experimental

The Raman spectra (figures 1, 2 and 3) of these compounds were recorded in a SPEX 'Ramalog' using the 4880 Å line of an argon ion laser (Spectra Physics Model 165) as the excitation line. IR spectra of $\text{Ni}_2P_4O_{12}$ and $\text{Zn}_2P_4O_{12}$ were recorded in a Perkin

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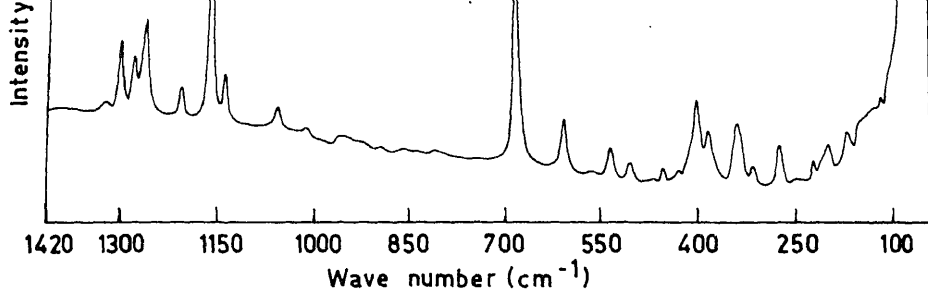


Figure 1. Raman spectrum of $\text{Fe}_2\text{P}_4\text{O}_{12}$.

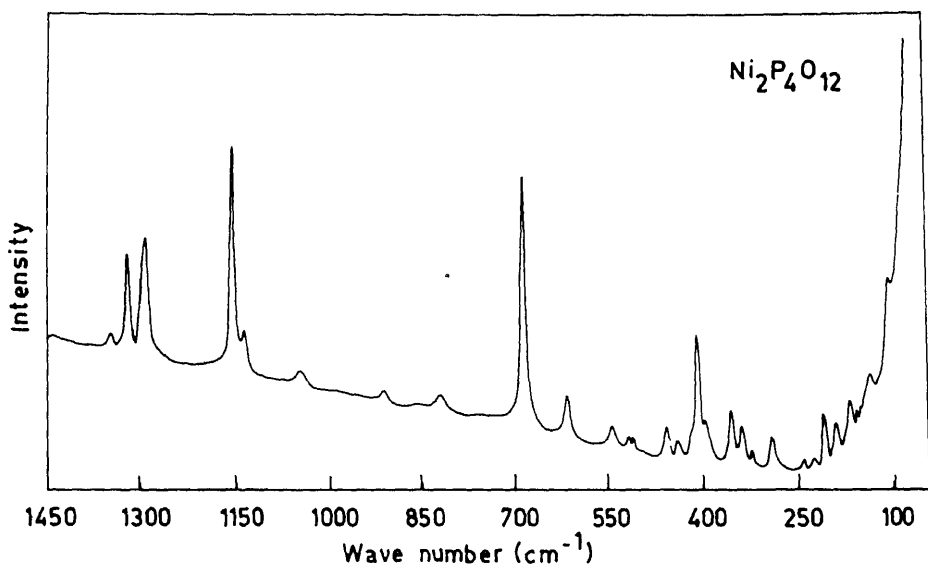


Figure 2. Raman spectrum of $\text{Ni}_2\text{P}_4\text{O}_{12}$.

Elmer 225 spectrophotometer with the samples as Nujol mulls. A Perkin Elmer 283 (spectrophotometer was used for $\text{Fe}_2\text{P}_4\text{O}_{12}$ (KBr pellet).

3. Factor group analysis

The crystal has a monoclinic structure with space group $C2/c$ (C_{2h}^6), with four formula units per crystallographic unit cell (Bagieu-Beucher *et al* 1976). The cations are located

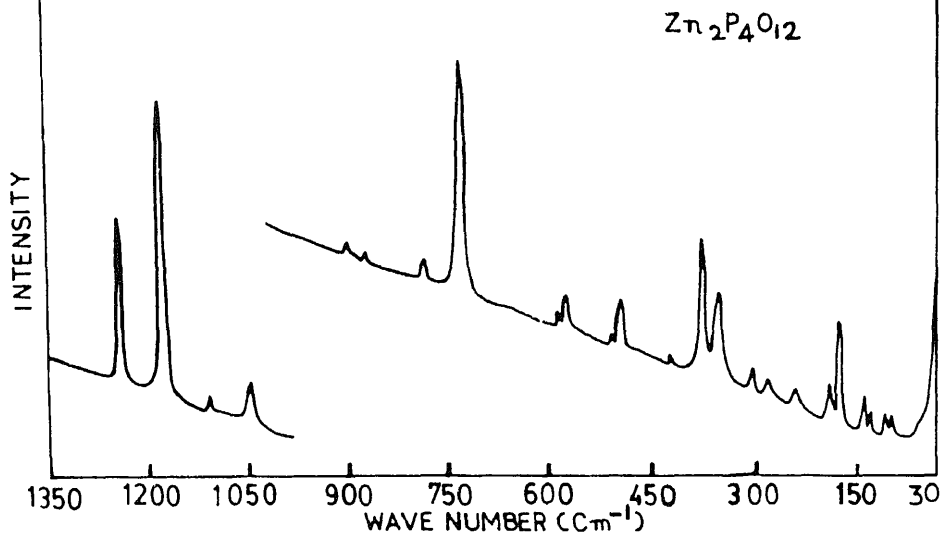
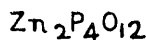


Figure 3. Raman spectrum of $\text{Zn}_2\text{P}_4\text{O}_{12}$.

at two different sites C_i and C_2 , and the phosphorus and oxygen atoms are in general positions. The environment of the phosphorus atom is tetrahedral. The $\text{P}_4\text{O}_{12}^{4-}$ ring is formed by joining the vertices of four distorted PO_4 tetrahedra. The divalent cations are octahedrally coordinated to the oxygen atoms. The distance between phosphorus and the bridging oxygen is slightly greater than that between phosphorus and terminal oxygen (sharing in the environment of the cation).

The factor group analysis with the standard correlation method (Fateley *et al* 1972), has been carried out for the Bravais unit cell. The two $\text{M}_2\text{P}_4\text{O}_{12}$ molecules in a Bravais unit cell give rise to 108 normal modes of vibrations, including the three acoustic modes. The total number of vibrations are distributed as follows:

$$\Gamma = (25A_g + 26B_g) + (27A_u + 27B_u) + (A_u + 2B_u).$$

The terms are, respectively, Raman active, IR active and acoustical vibrations. The normal vibrations of the anion with free ion symmetry C_i and C_{2h} are

$$\Gamma_{C_i} = 21 A_g + 21 A_u,$$

$$\Gamma_{C_{2h}} = 12 A_g + 9 B_g + 9 A_u + 12 B_u.$$

The correlations of the free ion symmetries C_i and C_{2h} with the factor group C_{2h}^6 are given in table 1. As the observed number of lines for $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$) are more than 42, the factor group method has to be used for the interpretation of their spectra. However a free ion model seems to be sufficient for explaining $\text{Zn}_2\text{P}_4\text{O}_{12}$ spectra (only 35 bands are observed).

Table 1. Correlation of the free ion symmetry C_i and C_{2h} , with the factor group C_{2h}^6 .

Free ion symmetry group C_i	Site symmetry group C_1	Factor group C_{2h}^6
21 A_g	A	A_g 21
		B_g 21
21 A_u		A_u 21
		B_u 21
Free ion symmetry group C_{2h}	Site symmetry group C_1	Factor group C_{2h}^6
12 A_g	A	A_g 21
9 B_g		B_g 21
9 A_u		A_u 21
12 B_u		B_u 21

4. Interpretation of the spectra

$\text{Fe}_2\text{P}_4\text{O}_{12}$: The frequencies are assigned on the basis of characteristic vibrations of PO_2^{2-} and P-O-P groups. The P-O bond in the PO_2^{2-} group is stronger than that in the P-O-P bridge. Consequently, the vibrational frequencies of the PO_2^{2-} group are expected to be higher than those for P-O-P bridge. The Raman lines observed at 1323, 1300, 1277, 1259 and 1206 cm^{-1} and the IR absorption at 1263 cm^{-1} are assigned to asymmetric PO_2^{2-} stretching modes. The PO_2^{2-} symmetric vibrations are observed at 1160, 1138 and 1057 cm^{-1} in the Raman and as a very weak band at 1115 cm^{-1} in the IR spectra. The Raman bands at 1015, 960 and 895 cm^{-1} and the IR band at 1030 cm^{-1} are assigned to the asymmetric P-O-P stretching mode. The symmetric P-O-P stretching vibrations are observed at 815 and 679 cm^{-1} in the Raman and at 730 and 705 cm^{-1} in the IR spectra.

The bending modes are expected in the region $600\text{--}450\text{ cm}^{-1}$ (PO_2^{2-} group) and $420\text{--}150\text{ cm}^{-1}$ (P-O-P bridge). The Raman lines at 608, 535, 505, 454 and 430 cm^{-1} and IR bands at 635, 571, 558, 525, 497, 476, 445 and 430 cm^{-1} are due to the deformation vibrations of PO_2^{2-} group. The bending vibrations for P-O-P are 400, 386, 338, 272, 221, 199 and 170 cm^{-1} in the Raman and 386, 358, 340, 310, 298 and 280 cm^{-1} in the IR spectra. As the metal oxygen stretching vibration (around 300 cm^{-1}) occurs in the P-O-P bending region (Gonzalez Diaz and Santos 1978), it is difficult to assign this vibration unambiguously. The very weak Raman line at 315 cm^{-1} may be due to metal oxygen stretching. The details of the observed spectra and their

Table 2. The fundamentals of $P_4O_4^{4-}$ ion in $M_2P_4O_{12}$ ($M = Fe, Ni, Zn$).

$Fe_2P_4O_{12}$			$Ni_2P_4O_{12}$			$Zn_2P_4O_{12}$		
Raman	IR	Species	Raman	IR	Species	Raman	IR	Species
1323 (2)	—	B_g	1345 (3)	—	B_g	—	1305 <i>vw</i>	A_u
1300 (14)	—	A_g	1318 (20)	—	A_g	—	1273 <i>w</i>	B_u
1277 (9)	—	B_g	—	1315 <i>vs</i>	A_u	1242 (31)	—	A_g
—	1263 <i>m</i>	B_u	—	1288 <i>vs</i>	B_u	—	—	$\nu_{asy} PO_2^{2-}$
1259 (20)	—	A_g	1289 (24)	—	A_g	—	—	
1206 (6)	—	A_g	—	—	—	—	—	
1160 (39)	—	A_g	1154 (46)	—	A_g	1179 (56)	—	A_g
1138 (9)	—	A_g	1138 (8)	—	A_g	—	1140 <i>m</i>	A_u
—	1115 <i>vw</i>	A_u	—	1112 <i>s</i>	A_u	1110 (3)	—	A_g
1057 (4)	—	B_g	—	—	—	—	1072 <i>s</i>	B_u
—	—	—	—	—	—	1050 (7)	—	B_g
—	1030 <i>w</i>	B_u	1046 (3)	—	B_g	—	1038 <i>s</i>	B_u
1015 (2)	—	B_g	—	1022 <i>s</i>	B_u	904 (3)	—	A_g
960 (2)	—	B_g	911 (2)	—	A_g	—	898 <i>s</i>	A_u
895 (1)	—	A_g	—	—	—	—	—	$\nu_{asy} POP$
815 (1)	—	A_g	820 (3)	—	A_g	875 (3)	—	A_g
—	730 <i>vs</i>	A_u	—	739 <i>vs</i>	A_u	788 (4)	—	B_g
—	705 <i>vs</i>	A_u	—	718 <i>vs</i>	A_u	734 (45)	—	A_g
679 (41)	—	A_g	686 (52)	—	A_g	—	708 <i>vs</i>	B_u
—	635 <i>w</i>	B_u	618 (8)	—	B_g	585 (3)	—	A_g
608 (9)	—	B_g	—	589 <i>m</i>	B_u	—	581 <i>s</i>	B_u
—	571 <i>m</i>	B_u	577 (2)	—	B_g	578 (7)	—	A_g
—	558 <i>s</i>	A_u	—	556 <i>s</i>	A_u	—	532 <i>vs</i>	A_u
535 (6)	—	B_g	542 (3)	—	B_g	506 (2)	—	A_g
—	525 <i>s</i>	A_u	—	525 <i>s</i>	A_u	497 (10)	—	A_g
505 (3)	—	A_g	517 (2)	—	A_g	—	459 <i>vs</i>	B_u
—	—	—	—	—	—	—	—	δPO_2^{2-}

Table 2. (Continued)

Fe ₂ P ₄ O ₁₂			Ni ₂ P ₄ O ₁₂			Zn ₂ P ₄ O ₁₂			Species	Assignment		
Raman	IR	Species	Raman	IR	Species	Raman	IR	Species				
—	497 s	A _u	511 (2)	—	A _g	—	382 m	B _u	δPO ₂ ²⁻			
—	476 m	B _u	—	504 vs	A _u	—	—	B _g				
454 (3)	—	A _g	—	463 w	B _u	381 (25)	—	A _g				
—	445 m	B _u	456 (6)	—	A _g	356 (18)	330 s	B _u				
430 (2)	—	B _g	441 (3)	—	B _g	—	—	A _g				
—	430 m	B _u	—	—	—	306 (5)	—	B _g				
—	—	—	—	—	—	284 (4)	—	A _u				
338 (10)	—	A _g	—	338 w	A _g	—	268 m	A _u			δPOP and M-O stretching	
315 (3)	—	A _g	324 (3)	—	A _g	—	—	A _u				
—	310 w	A _u	—	312 w	B _u	240 (4)	—	B _u				
—	298 w	B _u	—	298 w	B _u	—	212 s	A _g				
—	280 vw	B _u	291 (6)	—	B _g	191 (7)	—	A _g				
272 (8)	—	B _g	—	270 s	A _u	177 (22)	—	A _g				
221 (4)	—	A _g	—	250 vs	A _u	—	—	—				
199 (6)	—	A _g	240 (2)	—	A _g	—	—	—				
170 (5)	—	A _g	—	229 m	B _u	—	—	—				
—	—	—	—	219 m	B _u	—	—	—				
—	—	—	209 (10)	—	A _g	—	—	—				
—	—	—	190 (5)	—	A _g	—	—	—				
—	—	—	169 (7)	—	A _g	—	—	—				
—	—	—	157 (2)	—	A _g	—	—	—				
116 (3)	—	—	137 (2)	—	—	140 (6)	—	—	Lattice modes			
85 (1)	—	—	103 (1)	—	—	133 (3)	—	—	Lattice modes			
—	—	—	—	—	—	105 (4)	—	—	Lattice modes			
—	—	—	—	—	—	98 (3)	—	—	Lattice modes			

The numbers in parenthesis are relative intensities. vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

5. Results and discussions

The noncoincidence of the observed bands in IR and Raman spectra indicates that the anion is centrosymmetric. The few coincidences observed could be accidental. Though these samples contain the same anion, there are some differences in the number and frequencies of bands observed. A comparison of the spectra of $\text{Zn}_2\text{P}_4\text{O}_{12}$ with those of $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$) shows that the number of lines observed in each mode in $\text{Zn}_2\text{P}_4\text{O}_{12}$ is less than those in the other two. For example, the Raman band due to the asymmetric PO_2^{2-} stretching in $\text{Fe}_2\text{P}_4\text{O}_{12}$ splits into five lines, whereas only one is observed in $\text{Zn}_2\text{P}_4\text{O}_{12}$. Also, the IR absorption lines corresponding to the one at 708 cm^{-1} in $\text{Zn}_2\text{P}_4\text{O}_{12}$ are doublets in the other two compounds. The appearance of fewer vibrational bands in $\text{Zn}_2\text{P}_4\text{O}_{12}$ shows that the symmetry of the anion in this crystal is higher than that in $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$). Hence, it may be inferred that the anion has C_{2h} symmetry in $\text{Zn}_2\text{P}_4\text{O}_{12}$ and C_i in $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$).

The splitting of the asymmetric and symmetric vibrations of the PO_2^{2-} group into several components in $\text{Fe}_2\text{P}_4\text{O}_{12}$ suggests that the anion in $\text{Fe}_2\text{P}_4\text{O}_{12}$ is more distorted. In $\text{Fe}_2\text{P}_4\text{O}_{12}$ the low frequency end (895 cm^{-1}) and the high frequency and (1015 cm^{-1}) of the P–O–P asymmetric stretching region are, respectively, 16 and 31 cm^{-1} lower than those in $\text{Ni}_2\text{P}_4\text{O}_{12}$. This lowering is observed in other stretching and bending regions also. This suggests that the P–O bond strength in $\text{Fe}_2\text{P}_4\text{O}_{12}$ is slightly weaker than that in $\text{Ni}_2\text{P}_4\text{O}_{12}$. A similar comparison of the vibrational frequencies of the three compounds shows that the P–O bond strength is the highest in $\text{Zn}_2\text{P}_4\text{O}_{12}$ and lowest in $\text{Fe}_2\text{P}_4\text{O}_{12}$.

The anion has a centrosymmetric structure in all the three samples, C_{2h} in $\text{Zn}_2\text{P}_4\text{O}_{12}$ and C_i in $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$). The $\text{P}_4\text{O}_{12}^{4-}$ ion in $\text{Fe}_2\text{P}_4\text{O}_{12}$ is more distorted than in $\text{M}_2\text{P}_4\text{O}_{12}$ ($M = \text{Ni}, \text{Zn}$).

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Vibrational spectra and normal coordinate analysis for substituted trifluoromethyl benzenes

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Abstract. The polarised Raman spectra of the three isomeric trifluoromethyl benzonitriles have been recorded in the region $50\text{--}4000\text{ cm}^{-1}$. The near and far IR spectra of these compounds have been recorded in the region $200\text{--}4000\text{ cm}^{-1}$ and $33\text{--}700\text{ cm}^{-1}$ respectively. To check the vibrational assignments normal coordinate analysis was performed using general valence force field. Very good agreement has been achieved between the observed and the calculated fundamental frequencies. It has been possible to resolve the controversies about the assignments of the C-CF₃ stretching and CF₃ symmetric stretching modes in substituted trifluoromethyl benzenes. Vibrational assignments together with the force fields for three isomers are reported for the first time.

Keywords. Raman spectra; infrared spectra; vibrational spectra; normal coordinate analysis; force fields.

1. Introduction

In recent times, fluorinated compounds have become very important on account of their wide range applications. Fluorinated compounds are widely used as heat transfer fluids, chemical intermediates, polymers and so on. The present paper is in continuation of our studies of the vibrational spectra of substituted trifluoromethyl (TFM) benzenes Yadav and Singh (1984, 1985). In this paper, the results and analysis of the polarised Raman and infrared spectra of *o*-, *m*- and *p*-TFM benzonitriles are reported in the light of normal coordinate analysis. As far as we know, the vibrational spectra of the three isomeric TFM benzonitriles have not been reported so far. The aim of the present investigation is (i) to propose consistent vibrational assignments for the internal modes of the CF₃ group, (ii) to propose consistent vibrational assignments for the ring modes including the breathing and trigonal C-C-C in-plane bending modes, (iii) to see whether the CF₃ group behaves as a heavy substituent, (iv) to study the effect of CF₃ and CN groups in the *o*-, *m*- and *p*-positions of the substituted benzenes on their internal modes of vibrations and (v) to evaluate consistent force fields for the three isomeric TFM benzonitriles.

2. Experimental

All the three substances, *o*-, *m*- and *p*-TFM benzonitriles, were purchased from Alfa Ventron Corporation (USA) and were of specpure grade; *o*- and *m*-isomers are

colourless liquids at room temperature whereas the *p*-isomer is solid at room temperature and melts at $\approx 50^\circ\text{C}$ to form a colourless liquid. All the three substances were used as such for recording spectra.

The polarised Raman and near and far IR spectra of *o*- and *m*-TFM benzonitriles were recorded in the liquid phase at room temperature in the region $50\text{--}4000\text{ cm}^{-1}$ as described earlier (Yadav and Singh 1984, 1985). For recording the Raman spectra of *p*-TFM benzonitrile, the quartz sample cell was placed on a hot metal plate and the temperature was gradually increased till the sample had completely melted and its polarised Raman spectra were recorded in the molten state after a steady state had been achieved. The near IR spectrum of *p*-TFM benzonitrile was recorded in nujol mull.

Under the experimental conditions employed, measurements in all the three cases (Raman and near and far IR spectra) are accurate to $\pm 3\text{ cm}^{-1}$ and the resolution of the spectrometers was better than 2 cm^{-1} .

3. Normal coordinate analysis

Similar to the cases of isomeric trifluoromethyl benzaldehydes (Yadav and Singh 1984) and *p*-trifluoromethyl aniline (Yadav and Singh 1985) for the normal coordinate calculations, the *o*-, *m*- and *p*-TFM benzonitrile molecules have been assumed to belong to C_s point group. However, a local C_{3v} point group symmetry for the CF_3 group was assumed. The 42 normal modes of vibrations for each of the three isomeric TFM benzonitriles (total number of atoms = 16) are distributed as: $28a' + 14a''$ and in detail the distribution is as follows:

(i) Phenyl ring- $21a' + 9a''$ (ii) CF_3 group- $5a' + 4a''$ and (iii) CN group- $2a' + 1a''$. The distribution of normal modes for the phenyl ring is obvious and for the CF_3 group it has already been discussed in detail (Yadav and Singh 1984, 1985) and for the CN group, the distribution is given below:

C_s point group	a' species	a'' species
CN group	$\text{C}\equiv\text{N}$ stretch $\text{C}\equiv\text{N}$ in-plane bend	$\text{C}\equiv\text{N}$ out-of-plane bend

The symmetry coordinates for the phenyl ring part were constructed as per Whiffen (1955) and those for the CF_3 group as per Hollenstein and Günthard (1971). Because of some practical difficulties the CN group was taken to be a single mass point of equivalent atomic mass = 26 a.m.u. In the absence of any structural information for the three isomeric TFM benzonitriles, the geometrical parameters were taken from the work of Bürger *et al* (1982) for $\text{CF}_3\text{--CH=CH--CF}_3$ and Lide (1954) for $\text{C}_6\text{H}_5\cdot\text{CN}$ with hexagonal phenyl ring geometry. The calculations of *G* and *F* matrices and fundamental frequencies were made using the computer programme of Schachtschneider and Snyder (1963). General valence force field was used to calculate the fundamental frequencies. The force constants were transferred from the work of Yadav and Singh (1984, 1985) for substituted TFM benzenes and Kuwae and Machida (1979) for benzonitrile. The diagonal and off-diagonal force constants were initially adjusted by trial and error to give the best possible fit between the observed and calculated

force constants. The final sets of constants for *o*-, *m*- and *p*-TFM benzonitriles are given in table 1.

Results and discussion

The vibrational assignments for the observed frequencies have been proposed on the basis of magnitudes and relative intensities of the frequencies observed in the Raman

Table 1. Valence force constants for *o*-, *m*- and *p*-TFM benzonitriles.

Force constant number	Description and notation ^a	Value ^b		
		<i>o</i>	<i>m</i>	<i>p</i>
1	C-C stretch (R)	6.527	7.325	7.201
2	C-CF ₃ stretch (R_1)	4.840	4.343	4.946
3	C-CN stretch (R_2)	4.650	4.154	4.342
4	C-H stretch (R_3)	5.106	5.160	5.155
5	C-F stretch (R_4)	4.851	4.953	5.050
6	C-C-C angle bend (α)	0.943	0.934	1.014
7	F-C-F angle bend (α_1)	1.800	1.800	1.831
8	C-C-F angle bend (α_2)	1.212	1.215	1.210
9	C-CF ₃ out-of-plane bend (γ_1)	0.532	0.532	0.522
10	C-CN out-of-plane bend (γ_2)	0.265	0.300	0.286
11	C-H out-of-plane bend (γ_3)	0.300	0.265	0.254
12	C-C-C-C torsion (ϕ)	0.085	0.085	0.085
13	CF ₃ torsion (τ)	0.005	0.005	0.005
14	C-CF ₃ in-plane bend (β_1)	1.754	1.756	1.742
15	C-CN in-plane bend (β_2)	1.249	1.355	1.324
16	C-H in-plane bend (β_3)	0.950	0.953	0.946
17	(RR) ^o	1.155	0.758	0.651
18	(RR) ^m = (RR_1) ^m = (RR_2) ^m = (RR_4) ^m	-0.625	-0.350	-0.350
19	(RR) ^p = (RR_1) ^p = (RR_2) ^p = (RR_4) ^p	-0.134	0.350	0.350
20	$R_1 R_2 = (R_3 R_3)^o$	0.065	0.125	0.106
21	$R_4 R_4$	1.558	1.300	1.399
22	($\alpha\alpha$) ^o	-0.190	-0.134	-0.032
23	$\alpha_1 \alpha_1$	-0.113	0.247	0.235
24	$\alpha_2 \alpha_2$	0.649	0.664	0.420
25	$\gamma_1 \gamma_2 = (\gamma_3 \gamma_3)^o$	-0.008	-0.010	0.004
26	($\phi\phi$) ^o	0.007	-0.005	0.052
27	$\beta_1 \beta_2 = (\beta_3 \beta_3)^o$	-0.054	-0.009	0.013
28	($\beta_3 \beta_3$) ^m	-0.020	0.023	-0.021
29	($\beta_3 \beta_3$) ^p	0.062	0.043	-0.078
30	$R_i \alpha_i = R_i \alpha_{i+1}$	0.305	0.707	0.782
31	$R_i \beta_i = -R_i \beta_{i+1}$	-0.024	-0.062	-0.006
32	$-\alpha_{i+1} \beta_i = \alpha_{i+1} \beta_{i+2}$	-0.094	-0.158	-0.180
33	$-\phi_{i+1} \gamma_{i+1} = \phi_{i+1} \gamma_i$	0.020	0.018	0.011
34	(RR_1) ^o	-0.396	-0.682	0.276
35	(RR_2) ^o	-0.178	-0.224	0.395
36	$R_1 R_4$	1.184	1.192	1.365

^a *o*, *m* and *p* stand for *ortho*, *meta* and *para* interactions respectively; subscript *i*

analysis. In addition, assistance has also been taken from the vibrational assignments proposed for benzene derivatives containing CF_3 (Yadav *et al* 1982, Yadav and Singh 1982, 1984, 1985) and CN (Green 1961, Jakobsen 1965, Green and Harrison 1976, Kuwae and Machida 1979, Ram *et al* 1980-81) groups.

The discussion of the normal modes of vibrations of *o*-, *m*- and *p*-*ttm* benzonitriles can be divided into the following three groups: (i) phenyl ring modes, (ii) CF_3 group modes and (iii) CN group modes.

The phenyl ring modes for the *o*-, *m*- and *p*-*ttm* benzonitrile molecules are discussed separately whereas the CF_3 and CN group modes are discussed together for the three isomeric molecules.

Phenyl ring modes

o-*ttm* benzonitrile: The frequencies observed in the Raman and IR spectra of *o*-*ttm* benzonitrile together with their relative intensities, Raman depolarisation ratio, calculated fundamental frequencies and corresponding potential energy distributions of proposed vibrational assignments are presented in table 2. For assignments of most of the fundamental frequencies table 2 is self-explanatory. However, some of the phenyl ring modes deserve some discussion.

The Kekule mode gives rise to its characteristic frequency in the region 1000 – 1400 cm^{-1} for substituted benzenes and is easily assigned on account of its nearly pure $\text{C}=\text{C}$ stretching nature. In the present case, the frequency 1278 cm^{-1} is assigned to this mode.

For all *o*-disubstituted benzenes a strongly polarized Raman line at $\approx 1040\text{ cm}^{-1}$ is observed with good intensity and the corresponding IR band is observed with strong intensity. In the Raman spectrum of *o*-trifluoromethyl benzonitrile the frequency 1036 cm^{-1} is observed with strong intensity and low depolarisation ratio and the potential energy for this frequency contains appreciable contribution from $\text{C}=\text{C}$ stretching force constant. Similar to the case of *o*-trifluoromethyl benzaldehyde (Yadav and Singh 1984) this frequency (1036 cm^{-1}) is assigned to the ring breathing mode. In *o*-disubstituted benzenes the trigonal $\text{C}-\text{C}-\text{C}$ in-plane bending mode 12 of the benzene is sensitive to the position and nature of the substituents and is drastically reduced in magnitude due to its interaction with other planar modes. The frequency 1035 cm^{-1} is assigned to this mode. This frequency arises from strong interaction of the $\text{C}-\text{C}$ in-plane bending mode with the $\text{C}-\text{F}$ and $\text{C}-\text{C}$ stretching modes.

For all benzene derivatives containing CF_3 groups, a broad band near 1330 cm^{-1} appears with very strong intensity in the IR spectrum whereas in the Raman spectrum it is depolarised and appears with intensity ranging from weak to strong. Yadav and Singh (1984, 1985) have suggested that this frequency arises due to the $\text{C}-\text{CF}_3$ stretching mode for substituted *ttm* benzenes. In the present case, the frequency, 1320 cm^{-1} which arises from strong mixing of the $\text{C}-\text{CF}_3$ stretching mode with the $\text{C}-\text{C}$ and $\text{C}-\text{F}$ stretching, $\text{C}-\text{H}$ in-plane bending and CF_3 deformation and rocking modes, is assigned to the $\text{C}-\text{CF}_3$ stretching mode.

The $\text{C}-\text{CN}$ stretching frequency appears in the region 1100 – 1300 cm^{-1} for benzene derivatives containing a CN group. Kuwae and Machida (1979) have assigned the

Table 2. Observed and calculated fundamental frequencies for *o*-trifluoromethyl benzonitrile^a.

Observed					Calculated		Species	Proposed assignments
Raman	Infrared		CCl ₄ solution		Potential energy distribution ^b			
pure liquid	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	cm ⁻¹			
20 (0.32) <i>sh</i> <i>sh</i>		3210	12			A''	0 + 2241 + 964	
		3134	21			A'	0 + 2 × 1584	
		3104	28		3099 4 (97)	a'	C-H stretch	
		3070	26		3079 4 (98)	a'	C-H stretch	
					3052 4 (100)	a'	C-H stretch	
<i>sh</i>		3030	<i>sh</i>		3036 4 (101)	a'	C-H stretch	
		2980	41			A'	0 + 2241 + 743	
		2930	40			A'	0 + 1497 + 1454	
		2400	5			A'	0 + 1605 + 805	
		2254	<i>sh</i>			A'	0 + 1605 + 654	
100 (0.4) 2 (0.67)		2244	69			a'	C≡N stretch	
						A'	0 + 1036 + 1153; 0 + 1454 + 743	
						A'	0 + 1584 + 380	
		1960	13			A''	0 + 1201 + 771	
						A''	0 + 1114 + 743; 0 + 1201 + 654	
39 (0.69) 8 (0.54)		1850	15			A'	0 + 1175 + 557	
		1734	78			A''	0 + 964 + 771	
						A'	0 + 1320 + 318; 0 + 1150 + 493	
		1638	24			a'	C=C stretch	
		1602	58		1642 1 (62), 2 (25), 16 (12), 6 (8)	a'	C=C stretch	
5 (0.57)		1581	76		1596 1 (69), 16 (15), 3 (8), 6 (8)	a'	C=C stretch	
		1540	13			A'	0 + 1320 + 220	
		1491	76		1533 1 (65), 16 (33)	a'	C=C stretch	

Table 2. (Continued)

Raman	Observed		Infrared		CCl ₄ solution		Calculated		Species	Potential energy distribution	P. p. assignments
	Pure liquid	Rel int	Pure liquid	Rel int	CCl ₄ solution	Rel int	cm ⁻¹	cm ⁻¹			
	cm ⁻¹		cm ⁻¹		cm ⁻¹						
1 (p ^o)	1450	86	1455	42	1474	1.46 (0.15)			1	(H ₂) ⁺	(H ₂) ⁺
	1420	52							4	(H ₂) ⁺	(H ₂) ⁺
12 (p ^o 12)	1316	101B	1322	98	1335	16.35 (1.24 + 0.13)			6	(H ₂) ⁺	(H ₂) ⁺
12 (p ^o 13)	1274	91	1274	44	1290	1.74			7	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o)	1231	83	1233	13	1234	16.96 (1.54 + 0.13)			8	(H ₂) ⁺	(H ₂) ⁺
11 (p ^o 18)	1161	76	1207	36	1212	1.33 (0.27 + 0.13)			9	(H ₂) ⁺	(H ₂) ⁺
12 (p ^o 61)	1174	101B	1142	64	1226	4.44 (0.53 + 0.13)			10	(H ₂) ⁺	(H ₂) ⁺
					1237	1.26 (0.26 + 0.13)			11	(H ₂) ⁺	(H ₂) ⁺
					1244	1.34			12	(H ₂) ⁺	(H ₂) ⁺
					1254	1.54			13	(H ₂) ⁺	(H ₂) ⁺
					1274	1.74			14	(H ₂) ⁺	(H ₂) ⁺
					1289	1.91			15	(H ₂) ⁺	(H ₂) ⁺
12 (p ^o 22)	1312	94	1314	44	1331	1.74			16	(H ₂) ⁺	(H ₂) ⁺
12 (p ^o 28)	1312	94	1314	44	1331	1.74			17	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 29)	1306	77			1342	1.74			18	(H ₂) ⁺	(H ₂) ⁺
					1364	1.94			19	(H ₂) ⁺	(H ₂) ⁺
					1377	2.14			20	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 31)	1312	94			1389	2.34			21	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 33)	1312	94			1401	2.54			22	(H ₂) ⁺	(H ₂) ⁺
2 (p ^o 4)	1312	94			1414	2.74			23	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 45)	1312	94			1426	2.94			24	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 47)	1312	94			1438	3.14			25	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 49)	1312	94			1450	3.34			26	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 51)	1312	94			1462	3.54			27	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 53)	1312	94			1474	3.74			28	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 55)	1312	94			1486	3.94			29	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 57)	1312	94			1498	4.14			30	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 59)	1312	94			1510	4.34			31	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 61)	1312	94			1522	4.54			32	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 63)	1312	94			1534	4.74			33	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 65)	1312	94			1546	4.94			34	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 67)	1312	94			1558	5.14			35	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 69)	1312	94			1570	5.34			36	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 71)	1312	94			1582	5.54			37	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 73)	1312	94			1594	5.74			38	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 75)	1312	94			1606	5.94			39	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 77)	1312	94			1618	6.14			40	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 79)	1312	94			1630	6.34			41	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 81)	1312	94			1642	6.54			42	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 83)	1312	94			1654	6.74			43	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 85)	1312	94			1666	6.94			44	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 87)	1312	94			1678	7.14			45	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 89)	1312	94			1690	7.34			46	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 91)	1312	94			1702	7.54			47	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 93)	1312	94			1714	7.74			48	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 95)	1312	94			1726	7.94			49	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 97)	1312	94			1738	8.14			50	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 99)	1312	94			1750	8.34			51	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 101)	1312	94			1762	8.54			52	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 103)	1312	94			1774	8.74			53	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 105)	1312	94			1786	8.94			54	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 107)	1312	94			1798	9.14			55	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 109)	1312	94			1810	9.34			56	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 111)	1312	94			1822	9.54			57	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 113)	1312	94			1834	9.74			58	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 115)	1312	94			1846	9.94			59	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 117)	1312	94			1858	10.14			60	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 119)	1312	94			1870	10.34			61	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 121)	1312	94			1882	10.54			62	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 123)	1312	94			1894	10.74			63	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 125)	1312	94			1906	10.94			64	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 127)	1312	94			1918	11.14			65	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 129)	1312	94			1930	11.34			66	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 131)	1312	94			1942	11.54			67	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 133)	1312	94			1954	11.74			68	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 135)	1312	94			1966	11.94			69	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 137)	1312	94			1978	12.14			70	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 139)	1312	94			1990	12.34			71	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 141)	1312	94			2002	12.54			72	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 143)	1312	94			2014	12.74			73	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 145)	1312	94			2026	12.94			74	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 147)	1312	94			2038	13.14			75	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 149)	1312	94			2050	13.34			76	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 151)	1312	94			2062	13.54			77	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 153)	1312	94			2074	13.74			78	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 155)	1312	94			2086	13.94			79	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 157)	1312	94			2098	14.14			80	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 159)	1312	94			2110	14.34			81	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 161)	1312	94			2122	14.54			82	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 163)	1312	94			2134	14.74			83	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 165)	1312	94			2146	14.94			84	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 167)	1312	94			2158	15.14			85	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 169)	1312	94			2170	15.34			86	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 171)	1312	94			2182	15.54			87	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 173)	1312	94			2194	15.74			88	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 175)	1312	94			2206	15.94			89	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 177)	1312	94			2218	16.14			90	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 179)	1312	94			2230	16.34			91	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 181)	1312	94			2242	16.54			92	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 183)	1312	94			2254	16.74			93	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 185)	1312	94			2266	16.94			94	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 187)	1312	94			2278	17.14			95	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 189)	1312	94			2290	17.34			96	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 191)	1312	94			2302	17.54			97	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 193)	1312	94			2314	17.74			98	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 195)	1312	94			2326	17.94			99	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 197)	1312	94			2338	18.14			100	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 199)	1312	94			2350	18.34			101	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 201)	1312	94			2362	18.54			102	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 203)	1312	94			2374	18.74			103	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 205)	1312	94			2386	18.94			104	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 207)	1312	94			2398	19.14			105	(H ₂) ⁺	(H ₂) ⁺
1 (p ^o 209)	1312	94			241						

39 (0-26)	740	66	Beckman IR-11 ^c (Pure liquid)	725	6 (27), 3 (23), 1 (20), 5 (8)	<i>a'</i>	CF ₃ sym. stretch
	689	52				<i>A''</i>	0+555+127
9 (0-48)	651	86	<i>ms</i>	622	6 (49), 1 (8), 2 (8), 5 (8), 7 (7), 8 (5)	<i>a'</i>	C-C-C i.p. bend
2 ($\approx$ 1)	596	32	<i>m</i>			<i>A''</i>	0+318+284
6 (0-53)	555	84	<i>ms</i>			<i>a'</i>	C $\equiv$ N i.p. bend
	500	<i>sh</i>		519	12 (72), 9 (15), 8 (10)	<i>a''</i>	C-C-C-C torsion
				509	7 (60), 5 (53)	<i>a''</i>	CF ₃ asym. deformation
19 (0-38)	490	44		509	7 (59), 5 (54)	<i>a'</i>	CF ₃ asym. deformation
				444	12 (43), 10 (38), 11 (7)	<i>a''</i>	C-C-C-C torsion
	406	8	<i>mw</i>	438	6 (32), 3 (22), 14 (16), 1 (11), 3 (7), 6 (7)	<i>a'</i>	C-C-C i.p. bend
6 (0-38)	378	36	<i>w</i>	402	15 (37), 8 (19), 14 (16), 1 (11), 3 (7), 6 (7)	<i>a'</i>	C-CN i.p. bend
	362	<i>sh</i>				<i>a''</i>	C $\equiv$ N o.p. bend
17 (0-51)	318	55	<i>w</i>	280	6 (29), 2 (28), 8 (22), 7 (6)	<i>a'</i>	CF ₃ sym. deformation
	284	8	<i>mw</i>	290	8 (82), 12 (34), 10 (15), 11 (8)	<i>a''</i>	CF ₃ perpendicular rock
7 (0-72)	220	9	<i>vw</i>	226	8 (81), 15 (35), 1 (10), 2 (7)	<i>a'</i>	CF ₃ parallel rock
<i>sh</i> (dpt [†])			158	184	8 (55), 12 (49), 10 (15)	<i>a''</i>	C-CN o.p. bend
<i>sh</i> (pt [†])			135	131	8 (75), 14 (45), 15 (12)	<i>a'</i>	C-CF ₃ i.p. bend
49 (0-89)				121	12 (66), 8 (42), 9 (19)	<i>a''</i>	C-CF ₃ o.p. bend
			57	66	13 (88), 12 (10)	<i>a''</i>	CF ₃ torsion

Abbreviations used: Rel. int. = Relative intensity; Dep. = Depolarisation ratio; *sh* = shoulder; *B* = broad; *p*[†] = polarised; *dpt*[†] = depolarised; *i.p.* = in-plane; *o.p.* = out-of-plane; *sym.* = symmetric; *asym.* = anti-symmetric; *deform.* = deformation; *ms* = medium strong; *m* = medium; *w* = weak; *mw* = medium weak; *vw* = very weak; *vw* = very very weak.

Numbers outside the brackets are the force constant numbers defined in table 1 and those within the brackets are the corresponding contributions.

Frequencies observed in the spectrum of pure liquid, recorded on Beckman IR-11 spectrometer.

sh and *dpt* are used for those Raman lines for which depolarisation ratio could not be determined precisely.

1177 cm^{-1} frequencies in this mode. In the present case, although the region 1100–1300 cm^{-1} contains a number of frequencies, the potential energy distribution for only the 1201 cm^{-1} frequency has a contribution from the C–CN stretching force constant and therefore, the frequency 1201 cm^{-1} is assigned to the C–CN stretching mode.

4.1.b *m*-TFM benzonitrile: Table 3 presents the frequencies observed in the Raman and IR spectra of *m*-TFM benzonitrile together with their relative intensities, Raman depolarisation ratio, calculated fundamental frequencies and corresponding potential energy distribution and proposed assignments.

The Kekule mode, in the present case also, is assigned on account of the major contribution from the C–C stretching force constant to the frequency 1386 cm^{-1} .

In the region 640–1135 cm^{-1} , there are two strong Raman lines, namely, 736 and 1003 cm^{-1} either of which can be assigned to the ring breathing mode on the basis of only intensity considerations but as discussed later, the frequency 736 cm^{-1} is assigned to the CF_3 symmetric stretching mode and we assign the frequency 1003 cm^{-1} to the ring breathing mode, which is supported by normal coordinate analysis and also by the work of Singh and co-workers (Yadav and Singh 1982, 1984; Yadav *et al* 1982, Szostak 1979 and Katon *et al* 1980) for *m*-substituted benzenes.

As in the case of *o*-TFM benzonitrile, in this case also the trigonal C–C–C in-plane bending mode is considerably reduced and the frequency 809 cm^{-1} is assigned to this mode. This frequency arises from a mixing of the C–C–C in-plane bending mode with the C–F, C–C, C–CN and C– CF_3 , stretching and C–H in-plane bending modes.

The frequency 1332 cm^{-1} , observed with weak and very strong intensities in the Raman and IR spectra respectively, is a characteristic frequency of the CF_3 group and is assigned to the C– CF_3 stretching mode. As in the case of the *o*-isomer, in this case also this frequency arises from a mixing of the C– CF_3 stretching mode with other planar modes. On the basis of potential energy distributions and vibrational assignments made for benzene derivatives containing a CN group (Green 1961; Jakobsen 1965; Green and Harrison 1976; Kuwae and Machida 1979; Ram *et al* 1980–81) the frequency 1242 cm^{-1} is assigned to the C–CN stretching mode.

4.1.c *p*-TFM benzonitrile: The frequencies observed in the Raman and the IR spectra of *p*-TFM benzonitrile along with their relative intensities, depolarisation ratio of Raman lines, calculated fundamental frequencies and corresponding potential energy distributions and proposed assignments are presented in table 4.

In the present case the frequency 1391 cm^{-1} is assigned to the Kekule vibrations. This frequency arises from a mixing of a number of modes with the C–C stretching mode. However, the C–C stretching mode is dominantly involved in this frequency. The ring breathing mode for *p*-disubstituted benzenes has been assigned near 825 cm^{-1} by Yadav and Singh (1984, 1985) and Tripathi and Katon (1979). On the basis of Raman intensity, potential energy distribution and Raman depolarisation ratio, the frequency 806 cm^{-1} is assigned to the ring breathing mode for *p*-TFM benzonitrile. Although this mode is allowed in both the Raman and infrared spectra in the present case (point group- C_s), it has been observed in the infrared spectrum as a shoulder only. It appears that this mode retains its principal characteristics of the 992 cm^{-1} frequency of benzene (D_{6h} point group) where this mode is allowed in the Raman spectrum but forbidden in the IR spectrum.

Table 3. Observed and calculated fundamental frequencies for *m*-trifluoromethyl benzonitrile^a.

Observed				Calculated			Species	Proposed assignment
Raman	Infrared		CCl ₄ solution			Potential energy distribution ^b		
Pure liquid	Pure liquid							
cm ⁻¹	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	Rel. int.	cm ⁻¹		
3082	11 (0.43)	3440	21				A'	0 + 2241 + 1192
3023	1 (p†)	3200	sh				A'	0 + 2 × 1614
		3130	sh			3135 4 (96)	a'	C-H stretch
		3096	58			3082 4 (99)	a'	C-H stretch
						3079 4 (99)	a'	C-H stretch
						3028 4 (103)	a'	C-H stretch
		3020	sh				A''	0 + 2241 + 694
		2930	24				A'	0 + 2241 + 550; 0 + 1180 + 1003
		2785	15				A'	0 + 2241 + 471
		2710	15				A'	0 + 1391 + 1287
		2670	17				A'	0 + 2241 + 387
		2626	20				A''	0 + 1614 + 903
		2516	18				A'	0 + 1440 + 1071
		2470	14				A''	0 + 1614 + 860
							A'	0 + 1332 + 1145
		2370	17				A''	0 + 2241 + 135
		2282	sh				A''	0 + 1287 + 991
2238	80 (0.45)	2244	97				a'	C≡N stretch
2183-	0 (dp†?)	2185	sh				A''	0 + 1180 + 1003
		2066	17				A'	0 + 1332 + 735
		2030	17				A'	0 + 1483 + 550
							A''	0 + 1332 + 694
							A'	0 + 1332 + 650
		1980	24				A''	0 + 1287 + 694

Table 3. (Continued)

Observed				Calculated			Species	Proposed assignment
Raman		Infrared		Potential energy distribution ^b				
Pure liquid		Pure liquid		CCl ₄ solution				
cm ⁻¹	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	Rel. int.	cm ⁻¹		
		1923	29				A''	0 + 1332 + 592
		1862	24				A''	0 + 1003 + 860
							A'	0 + 1483 + 387
		1806	29				A'	0 + 1071 + 736
		1735	30				A'	0 + 1003 + 736
		1658	30				A'	0 + 1332 + 328
		1611	66				a'	C=C stretch
1616	9 (0.48)	1591	sh			1624 1 (70), 2 (16), 16 (14), 6 (7)	a'	C=C stretch
1597	7 (0.51)	1483	77	1491	29	1602 1 (93), 16 (14), 6 (7)	a'	C=C stretch
						1490 1 (73), 16 (16)	A'	0 + 809 + 650
		1461	sh				a'	C=C stretch
1443	2 (0.46)	1436	97	1442	47	1454 1 (106), 16 (15), 2 (6)	a'	C=C stretch
		1391	46	1393	29	1408 1 (54), 16 (30), 3 (13), 14 (6), 6 (5)	a'	C=C stretch (Kekule mode)
							a'	C-CF ₃ stretch
1337	10 (0.29)	1326	98B	1336	100	1325 16 (26), 7 (21), 2 (16), 5 (9), 7 (6), 8 (5)	a'	C-H i.p. bend
1288	1 (p)	1285	84	1290	35	1286 16 (59), 1 (29), 15 (5)	a'	C-CN stretch
	—	1247	45	1236	18	1235 1 (19), 16 (18), 3 (13), 5 (12), 6 (8), 8 (6), 7 (8)	A''	0 + 903 + 328
1228	sh						a'	CF ₃ asym. stretch
1193	11 (0.33)	1200	sh	1190	79	1191 5 (72), 7 (23), 16 (13), 1 (9), 8 (6)	a''	CF ₃ asym. stretch
1180	sh	1180	99B	1180	82	1200 5 (85), 7 (27), 8 (15), 9 (6)	a'	C-H i.p. bend
1140	1 (0.60)	1150	99B	1147	86	1155 16 (66), 1 (14)	A'	0 + 647 + 471
1113	2 (0.46)	1100	sh	1102	41		a'	C-H i.p. bend
1085	1 (p†)	1090	sh	1085	56	1092 16 (56), 1 (23), 3 (6), 5 (5)	a'	C-H i.p. bend
1071	1 (0.45)	1071	99	1071	40	1047 1 (56), 16 (35)	A'	0 + 550 + 471
1018	sh (p†)						a'	C-C stretch (ring breath)
1005	100 (0.29)	1000	62			1000 1 (29), 6 (49)	a'	

993	<i>sh</i>	988	<i>sh</i>	993	13	987	11 (78), 12 (36)	<i>a''</i>	C-H o.p. bend
937	0 (≈ 1)	917	<i>sh</i>	910	41	895	11 (70), 12 (20), 9 (16)	<i>A''</i>	0+650+286
		903	95			872	11 (79), 12 (35)	<i>A'</i>	0+694+222
862	1 (0-76)	858	95			829	6 (28), 5 (20), 1 (12), 3 (10), 16 (6), 2 (5)	<i>a''</i>	C-H o.p. bend
811	1 (<i>pr</i> ?)	806	98			771	12 (45), 11 (26), 9 (21)	<i>a''</i>	C-H o.p. bend
762	1 (<i>dpr</i> ?)	765	27			711	6 (27), 5 (21), 3 (17), 1 (10), 7 (5)	<i>a''</i>	C-H o.p. bend
737	42 (0-34)	734	100			694	11 (72), 12 (31)	<i>a''</i>	CF ₃ sym. stretch
		694	98					<i>a''</i>	C-C-C torsion
Beckman IR-11 ^c (Pure liquid)									
663	7 (0-46)	659	98	} 98	<i>s</i>	653	6 (69), 2 (9), 5 (6), 16 (5)	<i>a'</i>	C-C-C i.p. bend Fermi resonance between 652 cm ⁻¹ and 2 x 328
645	2 (0-71)	640	73						
593	1 (<i>dpr</i> ?)	591	27	27	<i>mw</i>	578	10 (35), 9 (24), 12 (23), 8 (11)	<i>a''</i>	C-C-C-C torsion
546	1 (<i>pr</i> ?)	553	82	82	<i>s</i>	484	7 (75), 5 (42)	<i>a'</i>	C≡N i.p. bend
471	9 (0-29)	471	62	62	<i>mw</i>	481	7 (84), 5 (35)	<i>a'</i>	CF ₃ asym. deform.
						449	12 (42), 10 (22), 11 (17)	<i>a''</i>	CF ₃ asym. deform.
388	3 (0-58)	386	25	25	<i>mw</i>	430	6 (32), 14 (15), 15 (15), 3 (12), 8 (20), 7 (9), 1 (5)	<i>a'</i>	C-C-C-C torsion
330	10 (0-28)	346	<i>sh</i>	<i>sh</i>		377	15 (30), 6 (25), 3 (19), 14 (11), 1 (10)	<i>a'</i>	C-C-C i.p. bend
		326	55	55		296	8 (35), 2 (27), 6 (23), 14 (11), 1 (11), 15 (8), 7 (9), 5 (9)	<i>a'</i>	C-CN i.p. bend
		286	10	10		270	8 (107), 12 (31), 11 (9)	<i>a'</i>	C≡N o.p. bend
		260	8	8				<i>a''</i>	CF ₃ sym. deform.
		232	4	4				<i>A'</i>	CF ₃ perpendicular ro
222	6 (<i>dpr</i> ?)					234	8 (53), 15 (27), 2 (23), 1 (13), 6 (13)	<i>a'</i>	0+2 x 135
163	4 (<i>pr</i> ?)					217	12 (55), 10 (24), 11 (12), 8 (10), 13 (7)	<i>a'</i>	CF ₃ parallel rock
137	31 (0-76)					147	8 (98), 14 (41), 15 (9)	<i>a'</i>	C-CN o.p. bend
						129	8 (69), 12 (29), 9 (25), 11 (10)	<i>a''</i>	C-CF ₃ i.p. bend
								<i>a''</i>	C-CF ₃ o.p. bend
								<i>A''</i>	0+387-285
						67	13 (89), 12 (6)	<i>a''</i>	0+330-285
								<i>A''</i>	CF ₃ torsion
									0+330-285

a, b, c See table 2, also for abbreviations.

Table 4. Observed and calculated fundamental frequencies for *p*-trifluoromethyl benzonitrile^a.

Observed				Calculated			Species	Proposed assignment
Raman	Infrared			Potential energy distribution ^b				
Pure liquid	Pure liquid	CCl ₄ solution						
cm ⁻¹	Rel. int. and dep.	cm ⁻¹	Rel. int.	cm ⁻¹	cm ⁻¹			
3088	10 (0.44)	3130	<i>sh</i>		3121 4 (97)		<i>a'</i>	C-H stretch
					3108 4 (97)		<i>a'</i>	C-H stretch
3018	1 (<i>pt</i>)	3070	33		3057 4 (101)		<i>a'</i>	C-H stretch
2240	100 (0.45)				3032 4 (101)		<i>a'</i>	C-H stretch
		2240	79				<i>a'</i>	C≡N stretch
		1970	24				<i>A''</i>	0+1124+836
		1945	19				<i>A'</i>	0+1409+547
		1920	25				<i>A''</i>	0+1183+739
		1838	19				<i>A''</i>	0+1183+644
		1790	14				<i>A''</i>	0+1051+739
		1720	11				<i>A'</i>	0+1183+547
		1670	10				<i>A'</i>	0+1124+547
1620	20 (0.61)	1612	27		1607 1 (94), 16 (19), 6 (8)		<i>a'</i>	C=C stretch
		1572	19		1592 1 (97), 16 (7), 6 (7), 14 (5)		<i>a'</i>	C=C stretch
1513	2 (0.5)				1514 1 (113), 16 (22)		<i>a'</i>	C=C stretch
		1409	69		1419 16 (46), 1 (37), 2 (19)		<i>a'</i>	C=C stretch
		1395	<i>sh</i>		1391 1 (56), 16 (27), 5 (10), 14 (10), 8 (6), 15 (5)		<i>a'</i>	C=C stretch (K mode)
1358	1 (<i>pt</i>)				1364 16 (64), 1 (11), 5 (9)		<i>a'</i>	C-H i.p. bend
1324	8 (0.4)	1320	97 <i>B</i>	100	1311 2 (39), 16 (20), 7 (13), 5 (9), 8 (9), 1 (7)		<i>a'</i>	C-CF ₃ stretch
1213	3 (<i>pt</i>)				1227 16 (44), 1 (14)		<i>a'</i>	C-H i.p. bend
1198	<i>sh</i>				1211 5 (87), 7 (27), 8 (15)		<i>a''</i>	CF ₃ asym. stretch
1186	34 (0.39)	1180	100 <i>B</i>	65	1184 1 (35), 3 (33), 6 (11), 15 (11)		<i>a'</i>	C-CN stretch

1138	1 (0-6)	1140	100B	1136	94 } 65 }	1145	5 (47), 8 (14), 23 (11), 16 (7), 9 (6)	a'	CF ₃ asym. stretch Fermi resonance bet 1124 and 644 + 488
1113	1 (0-50)	1104	110B	1100					
1074	8 (0-40)	1066	sh	1066	85	1090	16 (71), 1 (25)	a'	C-H i.p. bend
1043	1 (p)	1056	97	1050	sh	1054	1 (59), 16 (41)	a'	C-H i.p. bend
1023	3 (p)	1022	88	1019	86	1000	1 (49), 6 (40), 16 (10)	a'	C-C-C i.p. bend
968	1 (≈ 1)	961	sh			964	12 (73), 11 (67)	a"	C-H o.p. bend
912	1	920	sh					A"	0 + 784 + 141; 0 + 54
880	1	861	89			870	11 (52), 12 (39)	a"	C-H o.p. bend
		836	91			817	11 (85), 12 (44)	a"	C-H o.p. bend
811	48 (0-31)	800	sh			829	1 (30), 5 (18), 6 (16), 3 (9), 16 (8)	a'	C-C stretch (ring br)
786	11 (0-36)	781	sh			768	5 (30), 6 (23), 3 (15), 1 (7), 7 (7), 8 (5), 16 (5)	a'	CF ₃ sym. stretch
738	3 (0-77)	739	78			746	11 (76), 12 (32), 9 (5)	a"	C-H o.p. bend
645	10 (0-85)	643	28			658	12 (83), 9 (30), 8 (14), 10 (9), 5 (5)	a"	C-C-C-C torsion
		602	28			587	6 (105), 16 (5)	a'	C-C-C i.p. bend
543	4(0-63)	551	19					a'	C≡N i.p. bend
		488	11			485	7 (78), 5 (42)	a"	CF ₃ asym. deform.
						483	7 (85), 5 (35)	a'	CF ₃ asym. deform.
465	2 (≈ 1)					481	10 (43), 12 (41), 9 (16), 8 (14)	a"	C-C-C-C torsion
		441	6			435	6 (31), 3 (26), 2 (21), 1 (7), 7 (6), 5 (5)	a'	C-C-C i.p. bend
						417	12 (79), 11 (35)	a"	C-C-C-C torsion
						395	14 (35), 15 (31), 8 (31), 7 (8), 1 (6), 5 (5)	a'	C-CN i.p. bend
368	1 (≈ 1)	373	4					a"	C≡N o.p. bend
						319	12 (136), 8 (50), 10 (14)	a"	CF ₃ perpendicular r
294	33 (0-38)					298	6 (37), 2 (28), 7 (14), 8 (9), 3 (6), 1 (5)	a'	CF ₃ sym. deform.
220	2 (p†?)					245	15 (55), 8 (44), 1 (11)	a'	CF ₃ parallel rock
188	7 (dp†)					211	12 (111), 8 (45), 9 (12), 10 (8)	a"	C-CN o.p. bend
173	2 (p†?)					156	8 (60), 14 (46), 15 (6), 1 (5)	a'	C-CF ₃ i.p. bend
141	10 (dp†)					100	12 (80), 9 (19), 11 (17), 8 (13), 10 (5)	a"	C-CF ₃ o.p. bend
						20	13 (94), 12 (8)	a"	CF ₃ torsion

^{a, b} See table 2, also for abbreviations.

the same magnitude in the present case. The frequency 1023 cm^{-1} is assigned to this mode. The potential energy for this frequency has contributions from C–C in-plane bending, C–C stretching and C–H in-plane bending force constants. As in the case of the *o*- and *m*-isomers, the frequency 1322 cm^{-1} is a characteristic frequency of the CF_3 group and is assigned to the C– CF_3 stretching mode. This frequency arises from a mixing of the C– CF_3 stretching mode with other planar modes.

A polarised Raman line of medium-strong intensity is observed at 1183 cm^{-1} . The corresponding IR band of very strong intensity is also observed. The potential energy distribution for this frequency contains appreciable contribution from the C–CN stretching force constant and this frequency is assigned to the C–CN stretching mode.

4.2 CF_3 group modes

Under the point group C_{3v} , the CF_3 group gives rise to three non-degenerate modes (symmetric stretching, symmetric deformation and torsion) and three degenerate modes (anti-symmetric stretching, anti-symmetric deformation and rocking). On reduction of the symmetry from C_{3v} to C_s , each of the three degenerate modes splits up into two components. One component of each belongs to the symmetric species a' and the other one to the anti-symmetric species a'' . Hereafter, components under the species a' and a'' will be called symmetric and anti-symmetric components respectively.

For benzene derivatives containing CF_3 group(s), the CF_3 anti-symmetric stretching modes appear in the region $1100\text{--}1200\text{ cm}^{-1}$ with strong IR intensities but with varying Raman intensities. On the basis of potential energy distributions, relative intensities in the Raman and IR spectra and Raman depolarisation ratios, the frequencies 1175 , 1191 and 1124 cm^{-1} are assigned to the symmetric component of the degenerate CF_3 stretching mode for the three isomeric TFM benzonitriles respectively. The corresponding anti-symmetric components are assigned at 1197 , 1180 and 1198 cm^{-1} for the three isomers respectively.

The CF_3 symmetric stretching mode is expected to appear in the Raman spectrum with greater intensity as compared to the anti-symmetric CF_3 stretching modes. Yadav and Singh (1984, 1985) have assigned a frequency $\approx 750\text{ cm}^{-1}$ to the mode $\nu_s(\text{CF}_3)$ for isomeric TFM benzaldehydes. In the present case, the frequencies 743 , 736 and 785 cm^{-1} are observed with high intensities in the Raman spectra of the three isomeric TFM benzonitriles. Moreover, these frequencies have higher Raman intensities compared to the corresponding frequencies 1175 , 1191 and 1124 cm^{-1} , which have been assigned to the anti-symmetric CF_3 stretching mode. Therefore, the frequencies 743 , 736 and 785 cm^{-1} are assigned to the CF_3 symmetric stretching mode for the three isomers. Normal coordinate analysis also support the assignments of these frequencies to the CF_3 symmetric stretching mode.

The assignment of CF_3 anti-symmetric deformation mode (species a') is made easier due to the large contributions from the CF_3 deformation mode to the potential energy distributions for the frequencies 493 , 471 and 483 cm^{-1} for the three isomeric TFM benzonitriles respectively. These frequencies arise from strong mixing of CF_3 stretching and deformation modes. Similarly, the frequencies 509 , 481 and 488 cm^{-1} are assigned to the anti-symmetric components of the degenerate CF_3 deformation mode of the three isomers.

290–340 cm^{-1} . This frequency has good intensity in the Raman spectrum and usually medium intensity in the IR spectrum. In the Raman and IR spectra of nine related compounds* that we have studied, the magnitudes and relative intensities of absorption at this frequency match closely and compel us to believe that this frequency is essentially associated with the CF_3 group. In the Raman spectra of all the three isomeric TFM benzonitriles this frequency appears with medium intensity and is polarised. In the IR spectra for the *o*- and *m*-isomers this frequency has been observed with medium-strong intensity whereas for the *p*-isomer it has not been observed. In the light of potential energy distribution, relative intensities in the Raman spectra and Raman depolarisation ratios, the frequencies 318, 328 and 294 cm^{-1} are assigned to the CF_3 symmetric deformation modes for the three isomers respectively. Our assignment for this mode in the present case is in agreement with that of the isomeric TFM benzaldehydes (Yadav and Singh 1984) and *p*-TFM aniline (Yadav and Singh 1985).

The CF_3 rocking modes appear in the region 200–400 cm^{-1} . Moreover, the parallel rocking mode— $\rho_{\parallel}(\text{CF}_3)$ is observed to have lower magnitude compared to the perpendicular rocking mode— $\rho_{\perp}(\text{CF}_3)$ (Yadav *et al* 1982; Yadav and Singh 1982). In the present case, the frequencies 220, 232 and 220 cm^{-1} are assigned to the $\rho_{\parallel}(\text{CF}_3)$ mode for the three isomers respectively and the frequencies 282, 286 and 319 cm^{-1} are assigned to the $\rho_{\perp}(\text{CF}_3)$ mode.

Berney (1964a, b, 1969, 1971, 1973) has assigned the CF_3 torsional mode below 100 cm^{-1} for a number of compounds containing CF_3 group(s). In the present case, the frequencies 57, 72 and 20 cm^{-1} are assigned to this mode for the three isomeric TFM benzonitriles respectively.

4.3 CN group modes

For aromatic nitriles the $\text{C}\equiv\text{N}$ stretching frequency is very characteristic in magnitude and appears near 2240 cm^{-1} usually with strong intensities in both the Raman and IR spectra. The frequencies 2241, 2241 and 2240 cm^{-1} have been observed with very strong intensities in the Raman as well as the IR spectra of *o*-, *m*- and *p*-TFM benzonitriles respectively. These frequencies are assigned to the $\text{C}\equiv\text{N}$ stretching mode.

The $\text{C}\equiv\text{N}$ in-plane bending mode gives rise to its characteristic frequency in the neighbourhood of 550 cm^{-1} . In the case of benzonitriles- h_5 and d_5 Kuwae and Machida (1979) have assigned the frequencies 546 and 531 cm^{-1} to this mode. The frequencies 554, 536 and 550 cm^{-1} have been assigned to this mode by Ram *et al* (1980–81) for *o*-, *m*- and *p*-amino benzonitriles respectively. In the present case, the frequencies 557, 550 and 547 cm^{-1} are assigned to the $\text{C}\equiv\text{N}$ in-plane bending mode for the three isomers respectively.

Force field calculations on benzonitriles- h_5 and d_5 by Kuwae and Machida (1979) have shown that the frequencies 376 and 351 cm^{-1} in these arise from the $\text{C}\equiv\text{N}$ out-of-plane bending mode. The frequencies 362, 346 and 371 cm^{-1} are assigned to this mode for *o*-, *m*- and *p*-TFM benzonitriles respectively.

5. Summary and conclusions

Fairly consistent assignments for the internal modes of the CF_3 group for the three isomeric TFM benzonitriles are proposed. In all the three cases, the $\nu_s(\text{CF}_3)$ mode is observed to have greater intensity in the Raman spectra, compared to the $\nu_{as}(\text{CF}_3)$ modes. Similarly for the *m*- and *p*-isomers the $\delta_s(\text{CF}_3)$ mode is observed to have greater intensity in the Raman spectra than the $\delta_{as}(\text{CF}_3)$. However, for the *o*- isomer the $\delta_s(\text{CF}_3)$ mode has somewhat lower intensity in the Raman spectra than the $\delta_{as}(\text{CF}_3)$ modes.

For the *o*- and *m*-isomers, the ring breathing mode is observed to have nearly the same magnitude ($\approx 1000 \text{ cm}^{-1}$) as for benzene (992 cm^{-1}) whereas for the *p*-isomer, its magnitude is considerably reduced ($\approx 800 \text{ cm}^{-1}$). The C–C–C in-plane bending mode is assigned to considerably lower magnitude ($\approx 800 \text{ cm}^{-1}$) for the *o*- and *m*-isomers compared to benzene (1010 cm^{-1}) whereas for the *p*-isomer, this mode is observed to have nearly the same magnitude ($\approx 1020 \text{ cm}^{-1}$). Thus it appears that in the *o*- and *m*-positions of the substituents, the trigonal C–C–C in-plane bending mode strongly interacts with other planar modes whereas in the *p*-positions of the substituents, the ring breathing mode strongly interacts with other planar modes.

For all the three isomeric TFM benzonitriles, the C– CF_3 stretching frequency has been assigned at $\approx 1320 \text{ cm}^{-1}$. The assignment of this frequency with such a high magnitude to the C– CF_3 stretching mode suggests that the CF_3 group may not be assumed to be a heavy substituent as was suggested by Varsanyi (1969). The magnitude of the C–X stretching mode, where X is a heavy substituent, is expected to be less than 800 cm^{-1} (Varsanyi 1969). The present assignment is in agreement with the suggestion of D'Cunha and Kartha (1975). Consistent force fields for the three isomeric TFM benzonitriles have been evaluated for the first time.

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On the dissociation energy of MgH^+ molecule

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Abstract. The true potential energy curve for the electronic ground state, $X^1\Sigma^+$, of MgH^+ molecule has been constructed by the Rydberg-Klein-Rees method as modified by the method of Vanderslice *et al.* Empirical potential functions, of five-parameters by Hulburt and Hirschfelder, of three-parameters by Lippincott and others, and, of electronegativity by Szöke and Baitz, are examined for the adequacy to represent the true curve. The electronegativity function is found to be the best fitting function and the dissociation energy is estimated whose order is verified by the force constant.

Keywords. MgH^+ molecule; true potential energy curve, dissociation energy; electronegativity function; curve fitting method.

1. Introduction

The bond dissociation energy of a diatomic molecule is the most direct measure of the strength of the bond, and therefore of the stability of the chemical combination between the constituent atoms, that is, the very existence of the molecule. Astrophysicists, chemists and spectroscopists are therefore concerned with the determination of reliable values of dissociation energies for diatomic molecules.

Balfour (1972) reports that the $A^1\Sigma^+ - X^1\Sigma^+$ transition of MgH^+ is reasonably strong and it therefore seems possible that MgH^+ is present in a detectable amount in the solar spectrum.

The graphical Birge-Sponer extrapolation of vibrational levels in $X^1\Sigma^+$ and $A^1\Sigma^+$ states gives the dissociation energy D_0^0 value of MgH^+ as 2.08 eV (Huber and Herzberg 1979). Balfour (1972) has arrived at the D_0^0 value of MgH^+ as 2.23 eV from the ionization potential.

The curve fitting method is found to yield reliable values for the dissociation energies of a large number of diatomic molecules (Rajamanickam *et al.* 1982a, b; Narasimhamurthy and Rajamanickam 1983; Rajamanickam and Narasimhamurthy 1983; Rajamanickam 1985). The procedure consists of determining the D_e parameterised empirical potential function which best fits the true potential energy curve for the electronic ground state of the molecule. Many empirical potential functions have been proposed for this purpose. Of these functions given by Lippincott

2. True potential energy curve

Experimentally observed vibrational levels are used to construct the true potential energy curve. For the known vibrational levels, the Rydberg-Klein-Rees (R_{KR}) method gives the turning points by

$$r_{\pm} = [(f_v/g_v) + f_v^2]^{1/2} \pm f_v, \quad (1)$$

where f_v and g_v are calculated by the procedure of Vanderslice *et al* (1960). The molecular constants (Huber and Herzberg 1979) used in the present study are listed in table 1. In table 2, the computed values of the turning points are given for the molecular vibration in the electronic ground state of MgH^+ .

Table 1. Molecular constants for the electronic ground state, $X^1\Sigma^+$ of MgH^+ molecule.

ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	$\omega_e y_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	r_e (Å)	Electronegativities*	
						e_1	e_2
1699.1	31.935	-0.1882	6.387	0.18194	1.6519	1.2	2.1

Huber and Herzberg 1979; *Pauling (1960).

Table 2. Energy values from the EN function for MgH^+ molecule.

v	$r_{\pm}$ (Å)	$G(v)$ (cm^{-1})	$U(r)$ cm^{-1}		
			$D_e = 2.1 \text{ eV}$	$D_e = 2.15 \text{ eV}$	$D_e = 2.2 \text{ eV}$
0	1.8107	841.54	847.20	848.57	849.63
1	1.9498	2476.16	2494.52	2502.04	2508.77
2	2.0597	4045.20	4078.78	4088.20	4104.34
3	2.1597	5547.56	5571.89	5602.83	5631.93
4	2.2551	6982.12	6982.56	7030.40	7075.83
5	2.3494	8347.71	8307.42	8375.52	8440.57
6	2.4432	9643.24	9524.21	9615.22	9702.82
7	2.5397	10867.56	10650.91	10767.71	10880.55
8	2.6376	12019.55	11657.10	11801.28	11940.98
0	1.5220	841.54	833.74	832.69	832.02
1	1.4412	2476.16	2448.15	2443.90	2440.53
2	1.3917	4045.20	3992.58	3984.88	3978.04
3	1.3545	5547.56	5480.46	5468.79	5458.76
4	1.3245	6982.12	6908.03	6892.78	6879.37
5	1.2988	8347.71	8307.19	8288.23	8271.74
6	1.2766	9643.24	9652.93	9630.87	9611.13
7	1.2562	10867.56	11009.51	10984.12	10961.56
8	1.2381	12019.55	12317.75	12289.50	12264.16

Szöke and Baitz (1968) have constructed the electronegativity (EN) potential energy function, with the aid of parameters other than spectroscopic constants, to link different areas in chemical physics and they have replaced the force constant k_e of a diatomic molecule by an expression connected with the Pauling (1960) electronegativities e_1, e_2 as

$$k_e = d(e_1 e_2 D_e \times 1.60199 \times 10^{-12})^{1/2} r_e^{-1}, \quad (2)$$

And the EN function is in the form

$$U(r) = 8068.3 D_e [1 - \exp \{ -v(r - r_e)^2 / 2r \}] \\ \times [1 - a(b^2 v / 2r)^{1/2} (r - r_e) \exp \{ -(b^2 v / 2r_e)^{1/2} (r - r_e) \}], \quad (3)$$

where

$$v = de / (D_e \times 1.60199 \times 10^{-12})^{1/2},$$

$$d = 5.8883 \times 10^{-2} \mu_A \omega_e^2 r_e / (e_1 e_2 D_e \times 1.60199 \times 10^{-12})^{1/2},$$

$$a = 0.35 e^{1/2}, e = (e_1 e_2)^{1/2} \text{ and } b = 1.065.$$

4. Dissociation energy

For the constructed true potential energy curve, the energies $U(r)$ are calculated with the empirical potential functions by varying the D_e value. An average percentage deviation is determined between the calculated $U(r)$ and the experimental $G(v)$ values. The dissociation energy from any function is that value of D_e which gives the least deviation. The function leading to smallest deviation determines the dissociation energy of the molecule. The dissociation energy referred to $v = 0$ level is given by $D_0^0 = D_e - G(0)$.

This procedure is applied to determine the adequacy of the empirical potential functions (Lippincott *et al* 1961; Hulburt and Hirschfelder 1941; Szöke and Baitz 1968) to represent the electronic ground state of MgH^+ . D_e is varied over a range of 1.5 to 3.0 eV in steps of 0.05 eV. The EN function leads to the dissociation energy of MgH^+ , as the deviation is the least. Only relevant results of $U(r)$ are given in table 2. The estimated dissociation energy for the electronic ground state of MgH^+ is 2.05 ± 0.02 eV. The error indicated in the result takes into account the error of 1.04% involved in the curve fitting.

5. Conclusions

The results of the present study are significant since the EN function is suited for the MgH^+ molecule. The estimated dissociation energy $D_0^0 = 2.05 \pm 0.02$ agrees to within 2% of the value $D_0^0 = 2.08$ eV of Huber and Herzberg (1979). The force constant for the ground state of MgH^+ also indicates that the dissociation energy obtained in the present study is of the correct magnitude.

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Isothermal vapour-liquid equilibria for binary mixtures of *n*-octane with isomeric-butanols at 333.15 K

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Abstract. Isothermal vapour-liquid equilibrium (VLE) data were measured for the binary systems of *n*-octane with 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol at 333.15 K. The values of excess free energy, G_m^E , calculated are positive for all the systems. The results were correlated using Redlich-Kister and Wilson equations.

Keywords. Vapour-liquid equilibria; binary mixtures; excess free energy; alcohol-alkane interactions.

1. Introduction

Isothermal vapour-liquid equilibrium (VLE) studies for four binary systems of *n*-octane (1) and 1-butanol (2); *n*-octane (1) and 2-methyl-1-propanol (2); *n*-octane (1) and 2-butanol (2); and *n*-octane (1) and 2-methyl-2-propanol (2), at 333.15 K, were undertaken in the present work. The excess free energy of mixing, G_m^E , was calculated from these isothermal VLE data.

2. Experimental

2.1 Materials

Analytical reagent grade butanols were purified by fractional distillation over NaCl pellets, using a meter long column packed with glass helices. Reagent grade *n*-octane was purified over sodium. All the compounds were stored over 4A molecular sieves. The purity of the compounds as estimated by gas chromatography was better than 99.5 mole per cent. The densities of compounds are in good agreement with those reported in the literature (Riddick and Bunger 1970; Timmermans 1950).

2.2 Apparatus and procedure

The VLE data were determined using a modified Jones-Colburn recirculating system (Ammer *et al* 1956). The system pressure was adjusted to the desired value by means of a micrometer needle valve and a vacuum pump. The manometer readings were taken by means of a cathetometer accurate to within ± 0.01 mm. The ultimate system pressure was obtained after applying both the barometric and the gravitational corrections. The

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Table 1. Second virial coefficient (B) and molar liquid volume (V) of pure liquids at 333.15 K.

Compound	$B(\text{cm}^3 \text{mol}^{-1})$	$V(\text{cm}^3 \text{mol}^{-1})$
1-Butanol	-2360(-2364)*	95.2
2-Methyl-1-propanol	-2634(-2642)*	96.4
2-Butanol	-2288	96.0
2-Methyl-2-propanol	-1740	99.7
<i>n</i> -Octane	-3003	170.6

* Berro *et al* 1982.

temperature of the equilibrium chamber was measured accurately upto ± 0.1 K.

The vapour and liquid compositions were determined by the density method at 298.15 K for all the systems except for *n*-octane-2-methyl-2-propanol at 299.15 K. The uncertainty in the density measurements was less than 5×10^{-5} and in the mole fraction was less than 5×10^{-4} respectively.

The liquid phase activity coefficients (γ) were calculated according to the expression:

$$\gamma_i = (Py_i/P_i^s x_i) \exp \{ [(V_i - B_{ii})(P_i^s - P) + \delta_{12}(1 - y_i)^2 P]/RT \}, \quad (1)$$

where $i = 1, 2$; x, y are mole fractions of liquid and vapour respectively; P = solution pressure; P^s = vapour pressure of pure component; and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$.

The δ_{12} term was not taken into the calculations of γ , because of the large uncertainties involved in the calculated and actual values of B_{12} . The second virial coefficients (B) were calculated using Tsonopoulos equation (Tsonopoulos 1974), and are reported in table 1, along with the liquid molar volumes of pure components at 333.15 K. The values of second virial coefficients obtained for 1-butanol and 2-methyl-1-propanol are in agreement with those of Berro *et al* (1982).

The excess free energy was calculated using the equation:

$$G_m^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2). \quad (2)$$

3. Results and discussion

The P - x - y data measured at 333.15 K for the four systems along with the calculated values of γ_1, γ_2 and G_m^E are given in table 2.

The thermodynamic consistency of the experimental data was checked by Herington's (1952) equal area method. Even though the data have not been checked by the other computational methods (Cuncell and Hicks 1980; Christiansen and Fredenslund 1975), our data are thermodynamically consistent, being better than 1.5%, 3.0%, 1.8% and 2.0% for 1-butanol, 2-methyl-1-propanol, 2-butanol and 2-methyl-2-propanol systems respectively.

The excess free energy of mixing, G_m^E , is positive, throughout the concentration range (figure 1) and decreases with the branching of the alcohol. This behaviour may be due to hydrogen-bond breaking, molecular interactions and structural effects. Berro *et al*

Table 2. Isothermal vapour-liquid equilibrium data for *n*-octane(1)+ isomeric butanol (2) systems at 333.15 K.

x_1	y_1	$P(\text{mm Hg})$	γ_1	γ_2	G_m^E (J. mol ⁻¹)
<i>n</i> -Octane (1) + 1-butanol (2)					
0.0000	0.0000	59.20	—	1.000	—
0.0359	0.2075	72.22	5.316	1.001	170
0.0525	0.2601	76.80	4.854	1.010	258
0.1234	0.4159	91.71	3.936	1.028	536
0.1725	0.4800	99.61	3.515	1.052	717
0.2599	0.5226	105.87	2.697	1.147	996
0.3580	0.5534	110.13	2.155	1.286	1209
0.4742	0.5784	112.30	1.734	1.511	1324
0.5877	0.6002	112.72	1.457	1.835	1306
0.6557	0.6117	112.35	1.327	2.127	1233
0.7255	0.6293	110.93	1.218	2.512	1097
0.7883	0.6448	109.64	1.136	3.089	939
0.8297	0.6569	107.40	1.077	3.634	779
0.8802	0.6892	105.50	1.047	4.594	619
0.9266	0.7264	102.10	1.015	6.396	415
0.9450	0.7599	98.83	1.008	7.254	323
0.9670	0.8390	90.48	0.997	7.429	175
1.0000	1.0000	78.60	1.000	—	—
<i>n</i> -Octane (1) + 2-methyl-1-propanol (2)					
0.0000	0.000	92.4	—	1.000	—
0.0093	0.0372	96.61	4.916	1.015	83
0.0305	0.1107	102.07	4.713	1.012	173
0.1394	0.3171	123.0	3.559	1.052	611
0.2250	0.3859	130.64	2.828	1.115	881
0.3000	0.4168	133.74	2.344	1.199	1060
0.4791	0.4695	135.80	1.681	1.490	1231
0.5383	0.4808	135.00	1.555	1.605	1245
0.6405	0.5073	132.68	1.326	1.957	1170
0.6565	0.5127	131.23	1.294	2.003	1130
0.6710	0.5161	130.20	1.264	2.062	1095
0.7096	0.5389	129.60	1.223	2.182	1024
0.8095	0.5835	119.06	1.085	2.807	728
0.8341	0.5983	117.00	1.066	3.056	660
0.8920	0.6602	109.62	1.027	3.724	460
0.9450	0.7574	98.92	1.006	4.718	251
0.9600	0.7879	96.25	1.001	5.521	196
1.0000	1.0000	78.60	1.000	—	—
<i>n</i> -Octane (1) + 2-butanol(2)					
0.0000	0.0000	135.80	—	1.000	—
0.0392	0.0953	149.40	4.541	1.027	236
0.0640	0.1370	151.56	4.082	1.027	319
0.1155	0.2033	155.33	3.438	1.028	463
0.1837	0.2555	159.58	2.789	1.069	672
0.2445	0.2879	162.14	2.398	1.122	833
0.3097	0.3177	162.30	2.091	1.178	946
0.3922	0.3426	162.30	1.781	1.289	1054
0.4808	0.3643	160.82	1.531	1.446	1105
0.5847	0.3864	159.60	1.325	1.732	1088

Table 2. (Contd.)

x_1	y_1	$P(\text{mm Hg})$	γ_1	γ_2	G_m^E (J. mol ⁻¹)
0.7936	0.4737	144.83	1.089	2.717	758
0.8630	0.5228	137.13	1.047	3.517	588
0.9196	0.6187	118.34	1.007	4.141	334
0.8490	0.6931	108.53	1.004	4.824	233
0.9830	0.8441	92.06	1.003	6.244	97
1.0000	1.0000	78.6	1.000	—	—
<i>n</i> -Octane(1) + 2-methyl-2-propanol(2)					
0.0000	0.0000	289.60	—	1.000	—
0.0159	0.0187	290.51	4.208	1.000	64
0.0554	0.0506	289.33	3.256	1.004	192
0.1372	0.1080	284.51	2.761	1.016	424
0.2130	0.1452	280.20	2.356	1.052	616
0.3263	0.1846	273.87	1.913	1.146	841
0.4097	0.2053	266.70	1.652	1.242	925
0.4616	0.2200	261.43	1.542	1.311	957
0.5450	0.2424	249.56	1.374	1.439	938
0.6260	0.2632	236.92	1.237	1.619	868
0.7152	0.2857	224.57	1.116	1.956	747
0.8360	0.3400	200.03	1.016	2.799	504
0.8778	0.3866	182.41	1.006	3.192	407
0.9031	0.4168	172.93	1.001	3.631	348
0.9410	0.5231	142.81	1.000	4.038	229
0.9800	0.7652	101.80	1.007	4.196	100
1.0000	1.0000	78.6	1.000	—	—

energy of mixing of butanols and *n*-hexane, butanols and benzene and butanols and *n*-heptane systems respectively. They also observed that the G_m^E values were positive and decreased with the branching of the alcohol.

3.1 Correlation of data

The G_m^E data were fitted to the Redlich-Kister type polynomial equation:

$$G_m^E = x_1 x_2 \sum_0^2 A_n (x_1 - x_2)^n \quad (\text{J. mol}^{-1}). \quad (3)$$

Table 3. Fitting parameters of (3) along with standard deviations $\sigma(G_m^E)$.

System	A_0	A_1	A_2	$\sigma(G_m^E)$
<i>n</i> -Octane(1) + <i>n</i> -butanol(2)	5305.2	481.2	186.6	12.7
<i>n</i> -Octane(1) + iso-butanol(2)	4952.1	-322.2	328.3	22.1
<i>n</i> -Octane(1) + sec-butanol(2)	4387.9	86.9	827.1	22.7

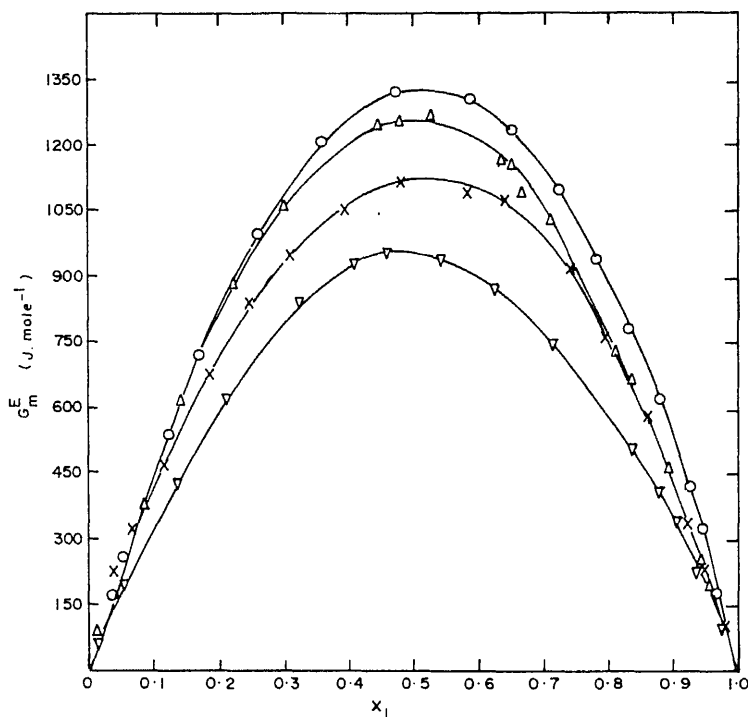


Figure 1. Excess free energy of mixing, G_m^E , at 333.15 K, for (O), *n*-octane (1) + 1-butanol (2); (Δ), *n*-octane (1) + 2-methyl-1-propanol (2); (x), *n*-octane (1) + 2-butanol (2); (∇), *n*-octane (1) + 2-methyl-2-propanol (2).

The least square constants along with $\sigma(G_m^E)$ are given in table 3. The G_m^E data were also correlated using Wilson's equation (Wilson 1964; Orye and Prausnitz 1965).

$$G_m^E/RT = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1). \quad (4)$$

The values of Λ_{12} and Λ_{21} along with $\sigma(G_m^E)$ are listed in table 4.

Table 4. The parameters of the Wilson equation (4) along with $\sigma(G_m^E)$.

System	Λ_{12}	Λ_{21}	$\sigma(G_m^E)$ (J. mol ⁻¹)
<i>n</i> -Octane(1) + 1-butanol(2)	0.3129	0.1883	20.6
<i>n</i> -Octane(1) + 2-methyl-1-propanol(2)	0.2565	0.3067	26.1
<i>n</i> -Octane(1) + 2-butanol(2)	0.3530	0.3093	26.5

4. Conclusions

From the above study the following conclusions may be drawn:

- (i) For all the four systems the excess free energy is positive due to hydrogen-bond breaking.
- (ii) Branching of the alkyl chain of alcohols makes a significant change in excess free energy.

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Second derivative analysis of S=O stretching band in Raman spectra of dimethyl sulphoxide in carbon tetrachloride and water

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Abstract. Raman spectra of solutions of DMSO (dimethyl sulphoxide) are studied in the S=O stretching region by second derivative analysis. Broad bands observed in the normal Raman spectra show well resolved components in the derivative plots. On the basis of the various components obtained in these plots for solutions of DMSO in carbon tetrachloride and water, existence of equilibria between various associated species, involving dipolar and hydrogen bonding interactions, is suggested. It is concluded that solutions of DMSO in CCl_4 may have monomers, cyclic and linear dimers and polymers, whereas its aqueous solutions show the existence of 1:1 and 1:2 hydrogen bonded complexes of water with DMSO in addition to smaller concentrations of monomers, dimers and polymers.

Keywords. Raman spectra; second derivative; hydrogen bonding; DMSO interactions.

1. Introduction

The high boiling point, the entropy of evaporation (higher than that of water) and cryoscopic investigations in benzene show that liquid dimethyl sulphoxide (DMSO) is highly associated (Lindberg *et al* 1961). Recent Raman spectral studies on solutions of DMSO in carbon tetrachloride and water by Singh and Krueger (1982) as well as Sastry and Singh (1984) show definite evidence for the associative properties of DMSO. It was shown that the broad bands in the S=O stretching region could be fitted by considering four components for solutions of DMSO in CCl_4 whereas the corresponding bands in aqueous solutions were fitted by considering five components. On the basis of these observations it was concluded that liquid DMSO is a mixture of monomers, cyclic dimers, linear dimers and higher polymers. When dissolved in CCl_4 the concentration of monomers and cyclic dimers increases. Solutions of DMSO in water show the presence of hydrogen bonded DMSO molecules with water in addition to the free and dimerised DMSO molecules.

Derivative spectroscopy was introduced in the early 50's by Hammond and Price (1953), Tannenbauer *et al* (1953), Morrison (1953) and Giese and French (1955). Recently Vandeginste and De Galan (1975), Talsky *et al* (1978), Maddams (1980), Maddams and Mead (1982), Hawkes *et al* (1982), Maddams and Southon (1982) and Barker and Fox (1980) have outlined methods to resolve IR and Raman spectral bands employing derivative spectroscopy (see appendix). As an extension to our work on the Raman spectra of solutions of DMSO in the S=O stretching region reported earlier (Sastry and Singh 1984), we report here the second derivative spectra to justify our model for the structure of liquid DMSO and its solutions.

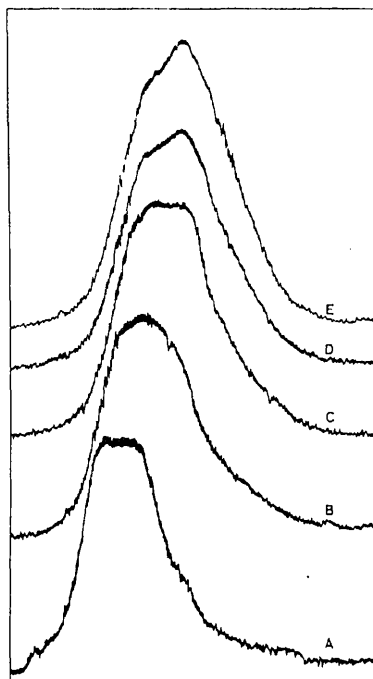
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2. Experimental and computational details

Details regarding spectral measurements and purity of chemicals used are as reported earlier (Sastry and Singh 1984). The second derivatives of the S=O stretching bands were computed using the 13 point polynomial method of Savitzky and Golay (1964). The calculations were performed on a Perkin Elmer Infrared Data system Model 3600 using a BASIC computer program developed in this laboratory.

3. Results and discussions

Raman spectra in parallel, polarized mode ($I_{||}$) of DMSO in CCl_4 at various concentrations and their second derivatives in the S=O stretching regions are shown in figures 1 and 2 respectively. The broad bands with weak shoulders in Raman spectra are found to resolve in the derivative spectra. The probable positions of the components, on the basis of the plots obtained from the derivative spectra for various solutions, are summarised in table 1. Pure DMSO shows three clear bands in the derivative spectrum at ≈ 1055 , 1041 , and 1029 cm^{-1} . Upon dilution in carbon tetrachloride a high frequency band starts rising at ≈ 1065 to 1070 cm^{-1} and the low frequency band at 1029 cm^{-1} shows significant lowering in intensity. The bands at ≈ 1055 and $\approx 1041\text{ cm}^{-1}$ also



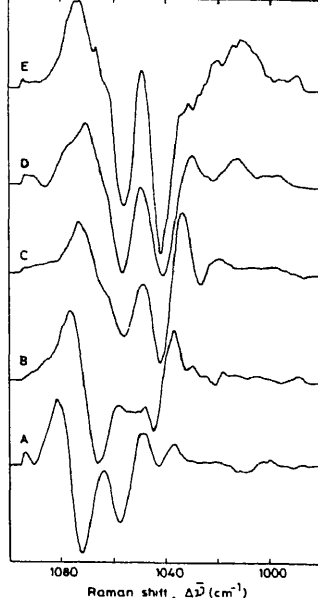


Figure 2. Second derivative plots for $I_{\parallel}$ spectra of solutions of DMSO in CCl_4 at different dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

Table 1. Spectral parameters of the component bands for the DMSO- CCl_4 system.

Mole fraction of DMSO	Present work	Results from Sastry and Singh (1984)			
	$\bar{\nu}(\text{cm}^{-1})$	$\bar{\nu}(\text{cm}^{-1})$	$\Delta\bar{\nu}_{1/2}^*(\text{cm}^{-1})$	Peak height	Integrated intensity (cm^{-1})
1.0	1029.0	1027.26	16.03	0.373	10.60
	1041.0	1042.06	12.43	0.631	13.89
	1055.0	1056.54	9.83	0.447	7.79
		1068.40	8.52	0.130	1.96
0.82		1028.70	20.41	0.263	9.61
	1040.0	1043.10	12.87	0.554	12.28
	1055.0	1057.50	10.77	0.382	7.29
		1069.72	12.01	0.105	2.23
0.50	1027.0	1028.51	18.79	0.261	8.70
	1042.0	1044.30	11.33	0.582	11.68
	1056.0	1057.56	9.45	0.422	7.03
	1062.0	1067.28	11.24	0.185	3.68
0.20		1025.93	15.05	0.200	5.35
	1044.5	1046.04	11.69	0.500	10.37
	1052.0	1057.50	11.25	0.341	6.84
	1066.0	1065.55	11.43	0.450	9.11
0.06		1023.87	18.02	0.099	3.17
		1048.11	11.85	0.334	7.02
	1057.5	1056.40	5.77	0.265	2.71
	1072.0	1068.03	12.00	0.862	18.34

show lowering in intensities. In all the cases the $\approx 1055 \text{ cm}^{-1}$ band is found to be lower in intensity than the $\approx 1041 \text{ cm}^{-1}$ band. The solution with 0.5 mf concentration shows all the four bands centered at $\approx 1062, 1056, 1042$ and 1027 cm^{-1} . These results show that DMSO solutions exhibit equilibria between species having Raman spectral bands at these four frequencies. In figure 3 is shown the second derivative spectrum of the isotropic Raman spectra of the above solutions for reference. As is well known the $I_{\parallel}$, $I_{\perp}$, I_{iso} and I_{aniso} spectra are respectively proportional to $(45\alpha^2 + 4\beta^2)$, $3\beta^2$, α^2 and β^2 where α and β represent the isotropic and anisotropic components of the polarisability tensor. The $I_{\perp}$ spectra directly give the I_{aniso} Raman components whereas I_{iso} components are obtained by subtracting $4/3 I_{\perp}$ from $I_{\parallel}$ spectra ($I_{\text{iso}} = I_{\parallel} - 4/3 I_{\perp}$).

The DMSO molecule is pyramidal in shape with two of the corners occupied by C atoms, one by an S atom and the fourth by an O atom. The S atom is sp^3 hybridised and the S–O bond is formed by an $sp^3 - p_x$ σ -overlap with a π -bond of the type $d_{xz} - p_z$ or $d_{yz} - p_y$ leading to a strongly polar S–O bond. As mentioned earlier (Sastry and Singh 1984, and references therein) associations through O–H bridging and S–H bridging appear improbable because of the low acidity of the C–H bond, while S–O bridging appears to be more probable because of the strong polar character of the S–O bond. Referring to the model based on the coexistence of equilibria between monomers, cyclic dimers, linear dimers/polymers in solutions of DMSO in CCl_4 the asymmetric S=O stretching bands in the Raman spectra of DMSO solutions were fitted with four Gaussian bands (Sastry and Singh 1984). It was argued, on the basis of relative intensities of the four components, that the band centered at $\sim 1070 \text{ cm}^{-1}$ belongs to the S=O stretching fundamental of monomers, whereas the two bands centered at ~ 1058 and 1040 cm^{-1} belong to out-of-phase and in-phase S=O stretching bands of

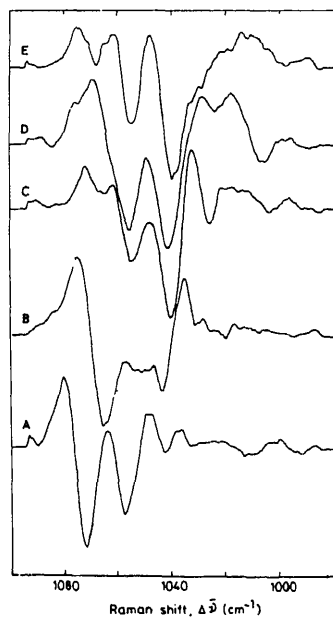


Figure 3. Second derivative plots for $I_{\perp}$ spectra of solutions of DMSO in CCl_4 at different

I_{iso} for a 0.5 m solution also shows four components as for $I_{\parallel}$ (figure 3). If the cyclic dimer with C_{2h} symmetry is considered then $I_{\parallel}$ and I_{iso} should show only one in-phase S=O stretching band. In case a slightly distorted cyclic dimer is considered without centre of inversion then $I_{\parallel}$ may show both in-phase and out-of-phase S=O stretching bands whereas I_{iso} should show only an in-phase band. Only in an extreme case where a distorted cyclic dimer has no effective symmetry element and belongs to C_1 symmetry both S=O stretching bands are expected to be observed in $I_{\parallel}$ and I_{iso} spectra. Two alternative assignments can therefore be proposed for the four components observed in $I_{\parallel}$ and I_{iso} spectra of DMSO solutions: (i) as suggested above the cyclic dimer is highly distorted having a C_1 symmetry thus leading to a high frequency band assigned to the monomer, the next two bands assigned to the cyclic dimer and the lowest frequency component assigned to the linear dimer/polymer species, (ii) in case the cyclic dimer has an inversion centre with or without slight distortion, the four components at ~ 1010 , 1055, 1040 and 1025 cm^{-1} can respectively be assigned to S=O stretching modes of monomer, cyclic dimer (in-phase), linear dimer and polymer species. The band due to the terminal S=O stretch of linear dimer is expected to be coincident with the monomer band.

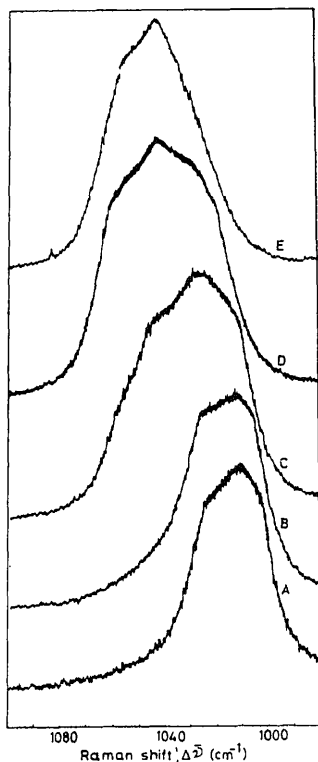


Figure 4. Raman spectra ($I_{\parallel}$) of solutions of DMSO in water at different dilutions (m 0.06; B-0.20; C-0.50; D-0.82; E-1.0 (taken from Sastry and Singh 1984).

In figure 4 are given the $I_{\parallel}$ bands in the S=O stretching region for several aqueous solutions of DMSO. The second derivative plots for these solutions for $I_{\parallel}$ and I_{iso} spectra are shown in figures 5 and 6 respectively. The probable positions of the components are given in table 2. In the previous publication it was suggested (Sastry and Singh 1984) that with increase in concentration of water a new band in the low frequency region of 1012 cm^{-1} starts rising in intensity such that for 0.06 mf of DMSO, 80% of the total intensity of the S=O stretching band is attributed to this component. The band was assigned to the S=O stretching mode of DMSO molecules hydrogen bonded to water molecules. The derivative plots for $I_{\parallel}$ spectra of these solutions show that the three main components of pure DMSO at $\sim 1055, 1041$ and 1029 cm^{-1} grow into four for 0.82 and 0.50 mf of DMSO in its aqueous solutions, the fourth band appearing at 1020 and 1012 cm^{-1} in the two solutions respectively. For 0.20 and 0.06 mf solutions the low frequency component is replaced by two components at ~ 1015 and 1005 cm^{-1} . It may be surmised that at lower concentrations of DMSO in aqueous solutions, two types of hydrogen bonded complexes may be present where one water molecule hydrogen

Table 2. Spectral parameters of the component bands for the DMSO-water system.

Mole fraction of DMSO	Present work	Results from Sastry and Singh (1984)			
	$\bar{\nu}(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\Delta\bar{\nu}_{1/2}^*(\text{cm}^{-1})$	Peak height	Integrated intensity (cm^{-1})
1.0	1029.0	1026.26	16.03	0.373	10.60
	1041.0	1042.06	12.43	0.631	13.89
	1055.0	1056.54	9.83	0.447	7.79
		1068.40	8.52	0.130	1.96
0.82	1020.50	1017.70	22.74	0.096	3.34
	1030.00	1025.00	12.14	0.325	7.00
	1043.00	1042.80	11.83	0.442	9.28
	1061.00	1059.00	10.36	0.334	6.14
		1072.80	10.75	0.037	0.72
0.50	1012.00	1014.90	17.11	0.178	5.38
	1027.50	1027.30	16.89	0.222	6.66
	1044.50	1044.90	12.12	0.182	3.91
	1057.50	1058.60	9.27	0.086	1.42
		1072.60	12.50	0.020	0.46
0.20	1008.50				
	1015.00	1010.30	14.08	0.249	6.69
	1027.00	1026.90	11.24	0.175	3.14
		1042.60	12.78	0.047	0.86
		1057.60	11.97	0.023	0.54
		1066.20	7.25	0.013	0.25
0.06	1005.00				
	1012.00	1012.00	17.78	0.268	8.40
	1025.50	1026.80	7.17	0.072	0.92
		1039.60	7.95	0.033	0.47
		1051.40	9.23	0.022	0.37
		1066.70	12.50	0.013	0.29

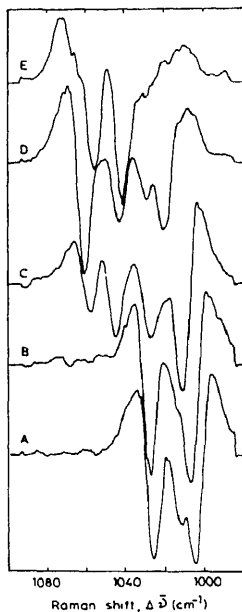


Figure 5. Second derivative plots for $I_{\parallel}$ spectra of solutions of DMSO in water at various dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

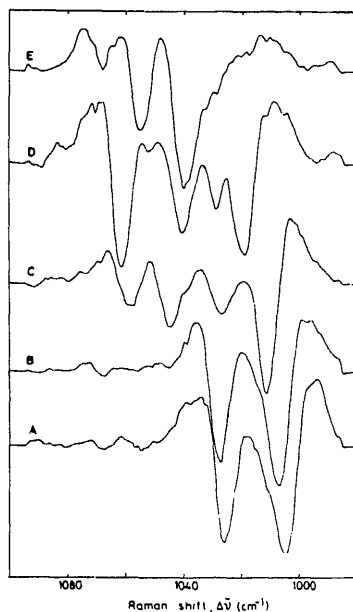


Figure 6. Second derivative plots for I_{iso} spectra of solutions of DMSO in water at various dilutions (mf) A-0.06; B-0.20; C-0.50; D-0.82; E-1.0.

bonds with one or two DMSO molecules, respectively, giving rise to asymmetrically and symmetrically hydrogen bonded water complexes. The two types of hydrogen bonded complexes may give rise to two low frequency components observed for dilute solutions of DMSO in water. The band components observed in the derivative spectra of I_{iso} are similar to those obtained for $I_{\parallel}$ derivative plots as expected from the analysis given above.

Acknowledgements

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Appendix. Derivative spectroscopy

The two common band shapes usually considered are the Lorentzian (Cauchy) and the Gaussian functions. Morrey (1968) reported the mathematical relationships between the first and higher derivatives of Lorentzian and Gaussian functions (table A1). In the case of Lorentzian or Gaussian functions the ratio of the half-width of the primary function to the half width of the second derivative is 1:0.33 i.e. it decreases to a third of its original value (Talsky *et al* 1978, and references therein). It has also been shown

Table A1. Relationships for derivatives of Lorentzian and Gaussian bands.

Band shape →	Lorentzian	Gaussian
Form	$I(\bar{\nu}) = I_0 [1 + X^2(\bar{\nu} - \bar{\nu}_0)^2]^{-1}$ $X_3 = 1/\text{HWHM}; \bar{\nu}_0 = \text{band centre}$ $dI(\bar{\nu})/d\bar{\nu}$	$I(\bar{\nu}) = I_0 \exp(-X^2(\bar{\nu} - \bar{\nu}_0)^2)$ $X_2 = (\ln 2)^{1/2}/\text{HWHM}; \bar{\nu}_0 = \text{band centre}$ $dI(\bar{\nu})/d\bar{\nu}$
1st derivative		
Root	$dI(\bar{\nu})/d\bar{\nu} = 0 = \bar{\nu}_0$	$dI(\bar{\nu})/d\bar{\nu} = 0 = \bar{\nu}_0$
Extremal values	$\bar{\nu}_0 \pm 0.5774 \text{ HWHM}$	$\bar{\nu}_0 \pm 0.8494 \text{ HWHM}$
2nd derivative	$d^2I(\bar{\nu})/d\bar{\nu}^2$	$d^2I(\bar{\nu})/d\bar{\nu}^2$
Root	$d^2I(\bar{\nu})/d\bar{\nu}^2 = 0 = \bar{\nu}_0 \pm 0.5774 \text{ HWHM}$	$d^2I(\bar{\nu})/d\bar{\nu}^2 = 0 = \bar{\nu}_0 \pm 0.8494 \text{ HWHM}$
Extremal values	$\bar{\nu}_0$ (minimum) $\bar{\nu}_0 \pm \text{HWHM}(\text{max})$	$\bar{\nu}_0$ (minimum) $\bar{\nu}_0 \pm 1.471 \text{ HWHM}(\text{max})$
Ratio of extremal values	$\text{Max}(\bar{\nu}_0 \pm \text{HWHM})/\text{min}(\bar{\nu}_0) = 0.25$	$\text{Max}(\bar{\nu}_0 \pm 1.471 \text{ HWHM})/\text{min}(\bar{\nu}_0) = 0.4462$
4th derivative	$d^4I(\bar{\nu})/d\bar{\nu}^4$	$d^4I(\bar{\nu})/d\bar{\nu}^4$
Root	$d^4I(\bar{\nu})/d\bar{\nu}^4 = 0 = \bar{\nu}_0 \pm 0.3250 \text{ HWHM}$	$d^4I(\bar{\nu})/d\bar{\nu}^4 = 0 = \bar{\nu}_0 \pm 0.6302 \text{ HWHM}$
Extremal values	and $\bar{\nu}_0 \pm 1.3764 \text{ HWHM}$ $\bar{\nu}_0 \pm 0.5774 \text{ HWHM}$ (minimum) $\bar{\nu}_0(\text{max}), \bar{\nu}_0 \pm 1.732 \text{ HWHM}$	and $\bar{\nu}_0 \pm 1.9828 \text{ HWHM}$ $\bar{\nu}_0 \pm 1.150 \text{ HWHM}$ (minimum) $\bar{\nu}_0(\text{max}), \bar{\nu}_0 \pm 2.4264 \text{ HWHM}$
Ratio of extremal values	$\text{Min}(\bar{\nu}_0 \pm 0.5774 \text{ HWHM})/\text{max}(\bar{\nu}_0) = 0.4219$	$\text{Min}(\bar{\nu}_0 \pm 1.150 \text{ HWHM})/\text{max}(\bar{\nu}_0) = 0.6182$

HWHM-half width at half maximum.

The criterion for a peak to be observed is that the first derivative $dI(\bar{\nu})/d\bar{\nu} = 0$, and the second derivative $d^2 I(\bar{\nu})/d\bar{\nu}^2$ is negative. Morrey (1968) used the following conditions to define a peak:

$$d^2 I(\bar{\nu})/d\bar{\nu}^2 < 0; d^3 I(\bar{\nu})/d\bar{\nu}^3 = 0; d^4 I(\bar{\nu})/d\bar{\nu}^4 > 0.$$

On the higher derivatives, the adjacent bands have much less effect because of the narrower half-widths of the derivatives.

Westerburg (1969) defined two limits for the overlap of two component bands called the shoulder limit and the detectability limit. The point at which two peaks overlap to such a degree that the valley between them just disappears is defined as the shoulder limit and is expressed by the following equations:

$$dI(\bar{\nu})/d\bar{\nu} = d^2 I(\bar{\nu})/d\bar{\nu}^2 = 0.$$

The detectability limit occurs, when an inflection point of the profile and the maximum of the minor peak coincides, which is expressed mathematically by the following equation:

$$d^2 I(\bar{\nu})/d\bar{\nu}^2 = d^3 I(\bar{\nu})/d\bar{\nu}^3 = 0.$$

The shoulder and detectability limits of overlapping Gaussian and Lorentzian bands of various half-widths and intensity ratios have been reported by Vandeginste and De Galan (1975).

Maddams and Mead (1982) and Maddams and Southon (1982) studied the effects of background and half-widths of component bands on the measurement of derivatives. Baker *et al* (1978) have examined the problem in context with the quantitative use of derivative spectra to characterize band shapes, following the procedure of Grushka and Monacelli (1972). They pointed out that the intensity ratio of the positive and negative lobes of the second derivative is a measure of the band shape: it is found to be 0.250 for a Lorentzian profile and 0.446 for a Gaussian band.

In the present study, for calculation of second derivatives we have used the convolution least squares method introduced by Savitsky and Golay (1964). The method provides a combined approach to smoothing and derivatization. A set of data points, collected at equal abscissal intervals is fitted to a polynomial by a least squares calculation. This set of points is moved forward sequentially by one data point until the whole spectrum has been covered. The degree of the polynomial, n , sets the limit to the highest derivative that may be obtained. This method is mathematically equivalent to convoluting the original data with a numerical function, and Savitzky and Golay (1964) have provided values for these functions for polynomials of various degrees and derivatives of various orders. The various mathematical steps involved in the convolution least squares method can be found in the pioneering work of Savitzky and Golay (1964). Steinier *et al* (1972) have subsequently noted errors in some of these numerical values and have supplied corrected tables. In our calculation we have used a 13 point quadratic polynomial for second derivative calculations.

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Intermolecular energy calculations on 4'-nitrophenyl, 4-hexyloxybenzoate—a mesogenic compound

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Abstract. Intermolecular interaction energies between a pair of 4'-nitrophenyl, 4-hexyloxybenzoate (NPHB) molecules, have been calculated. CNDO/2 method has been employed to compute the net atomic charge and atomic dipole components at each atomic centre. A second order perturbation theory with multicentered-multipole approximation has been used to evaluate the energies corresponding to the stacked and in-plane lateral interactions between a pair of the molecules. An attempt has been made to discuss the results in the light of experimental evidences.

Keywords. Mesomorphism; intermolecular energy; stacking interaction; multicentered-multipole.

1. Introduction

Role of molecular forces and conformational properties on mesomorphic behaviour have attracted the attention of a large number of workers (Gray 1962; Chandrasekhar *et al* 1970; Photinos 1979; de Gennes 1975; Dong *et al* 1981; Tokita *et al* 1981; Berges and Perrin 1981; Perrin and Berges 1981, 1982). The successful application of quantum mechanical methods for discussion of the liquid crystalline behaviour of anisaldehydeazine (Sanyal *et al* 1984) and biphenyls (Sanyal *et al* 1985) encouraged us to examine the validity of these methods for other systems. 4'-nitrophenyl, 4-hexyloxybenzoate (NPHB) has been chosen from the homologous series of 4'-nitrophenyl, 4-*n*-alkoxybenzoates. In this series, homologues upto pentyloxy are pure nematogenic, except the first two members, while homologues after octyloxy are all pure smectogenic (Griffin *et al* 1978). Therefore, it is pertinent to study this model system as it shows both the smectic and nematic mesophases. During the heating cycle, NPHB shows crystal to nematic transition at 55°C and nematic to isotropic at 57.5°C, while in the cooling cycle nematic to smectic transition takes place at 40°C (Griffin *et al* 1978). The molecular geometry has been constructed on the basis of the published crystallographic data (Kaiser *et al* 1980). The CNDO/2 method (Pople and Beveridge 1970) has been employed to compute net atomic charge and dipole at each atomic centre. Using this quantum mechanical charge distribution and second order perturbation treatment with multicentered-multipole approximation (Rein 1978; Claverie 1978), the stacking as well as in-plane interaction energy values have been evaluated. In this paper, only the lowest energy configurations have been reported and used to discuss molecular ordering, mesomorphic behaviour and related parameters of NPHB molecules.

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Caillet *et al* (1976) for intermediate range interactions has been used to evaluate the intermolecular interaction energy between a pair of NPHB molecules. The total interaction energy (E_{TOT}) is expressed as

$$E_{TOT} = E_{EL} + E_{POL} + E_{DISP} + E_{REP}$$

where E_{EL} , E_{POL} , E_{DISP} and E_{REP} are electrostatic, polarization, dispersion and repulsion energy terms respectively. Electrostatic energy (Rein 1973) is again calculated upto dipole-dipole term as

$$E_{EL} = E_{QQ} + E_{QMI} + E_{MIMI}$$

where E_{QQ} , E_{QMI} and E_{MIMI} are monopole-monopole, monopole dipole and dipole-dipole interaction energy terms respectively. The details of the formalism may be found elsewhere (Sanyal *et al* 1984). Net atomic charges and dipoles have been computed by the CNDO/2 method (Pople and Beveridge 1970).

Minimum energy configuration between a pair of NPHB molecules has been obtained by varying the position of one molecule along the rectangular coordinate axes with a simultaneous rotation keeping the other fixed. The same process has been repeated after inversion of the molecule. Accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to the other has been achieved. The stacking and in-plane configurational interaction energies have been minimized separately.

All the computations have been carried out on a CDC 'Cyber' computer at TIFR, Bombay.

3. Results and discussion

The molecular geometry of the NPHB molecule is shown in figure 1 while the net charge and dipoles at each atomic centre are listed in table 1. The total dipole moment, its components and the binding energy of the molecule are given in table 2. The lowest energy configurations obtained for stacking and in-plane interactions have been shown in figures 2 and 3 respectively. The corresponding energies and various contributing terms are listed in table 3.

Figure 2 shows two molecules of NPHB which are stacked one above the other 4.20 Å apart with one molecule inverted in its plane and laterally displaced with respect to the

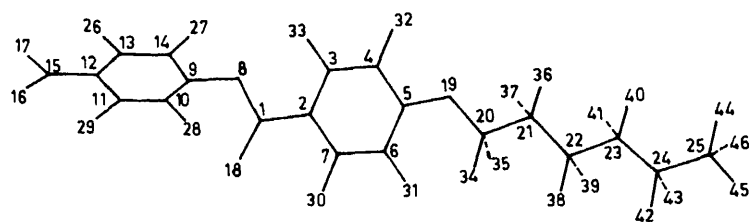


Figure 1. Molecular geometry of NPHB molecule with various atomic index numbers.

Table 1. Atomic charges and dipoles of NPHB molecule.

Atom	No.	Charge	Atomic dipole moments		
			X	Y	Z
C	1	0.400	-0.232	0.167	-0.002
C	2	-0.073	0.056	-0.023	-0.018
C	3	0.053	0.048	-0.131	-0.003
C	4	-0.063	-0.090	-0.162	-0.008
C	5	0.210	0.201	0.028	-0.006
C	6	-0.067	-0.068	0.154	0.004
C	7	0.056	0.083	0.124	0.000
O	8	-0.264	-0.809	-0.977	-0.030
C	9	0.203	0.162	-0.020	-0.008
C	10	-0.032	-0.102	0.117	-0.155
C	11	0.038	0.090	0.098	-0.183
C	12	0.022	-0.189	0.038	-0.012
C	13	0.039	0.033	-0.122	0.180
C	14	-0.038	-0.139	-0.070	0.142
N	15	0.467	-0.026	0.049	-0.054
O	16	-0.352	0.728	0.408	-1.123
O	17	-0.321	0.516	-0.641	1.145
O	18	-0.320	0.777	1.133	0.043
O	19	-0.226	-0.678	-1.140	0.202
C	20	0.153	-0.085	0.235	-0.036
C	21	-0.001	-0.055	-0.120	0.034
C	22	0.021	0.004	0.111	-0.045
C	23	0.019	-0.026	-0.076	0.042
C	24	0.024	0.040	0.083	-0.045
C	25	-0.007	-0.163	-0.030	0.033
H	26	0.025	0.000	0.000	0.000
H	27	0.019	0.000	0.000	0.000
H	28	0.023	0.000	0.000	0.000
H	29	0.028	0.000	0.000	0.000
H	30	0.003	0.000	0.000	0.000
H	31	0.008	0.000	0.000	0.000
H	32	0.014	0.000	0.000	0.000
H	33	-0.000	0.000	0.000	0.000
H	34	-0.016	0.000	0.000	0.000
H	35	-0.017	0.000	0.000	0.000
H	36	0.008	0.000	0.000	0.000
H	37	0.005	0.000	0.000	0.000
H	38	-0.007	0.000	0.000	0.000
H	39	-0.006	0.000	0.000	0.000
H	40	-0.007	0.000	0.000	0.000
H	41	-0.005	0.000	0.000	0.000
H	42	-0.008	0.000	0.000	0.000
H	43	-0.008	0.000	0.000	0.000
H	44	0.001	0.000	0.000	0.000
H	45	-0.003	0.000	0.000	0.000
H	46	0.001	0.000	0.000	0.000

Table 2. Dipole moment distribution, total^a and binding^b energy of NPHB molecule.

Components	<i>X</i>	<i>Y</i>	<i>Z</i>
Densities	3.64	-0.38	0.05
<i>sp</i> *	0.08	-0.77	0.10
<i>pd</i> *	0.00	0.00	0.00
Total	3.72	-1.15	0.15

Total energy = -255.095017 atomic unit.

Binding energy = -23.060098 atomic unit.

Total dipole moment = 3.89374 debyes.

^a Total energy corresponds to the sum of atomic as well as electronic energies of all the constituents of the molecule in the equilibrium geometry.

^b Binding energy of a molecule is the difference between the total energy of the equilibrium molecular geometry and the sum of the atomic energies of the constituent atoms.

* *sp* hybridization moment.

** *pd* hybridization moment.

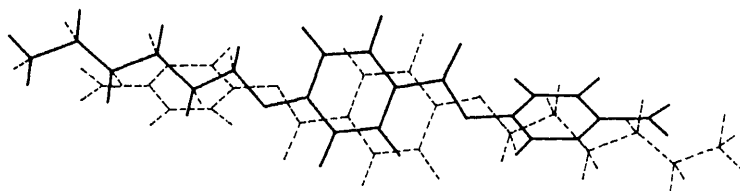


Figure 2. Lowest energy stacked complex of two antiparallel NPHB molecules having energy -12.25 kcal/mole and inter-planar separation of 4.20 Å.

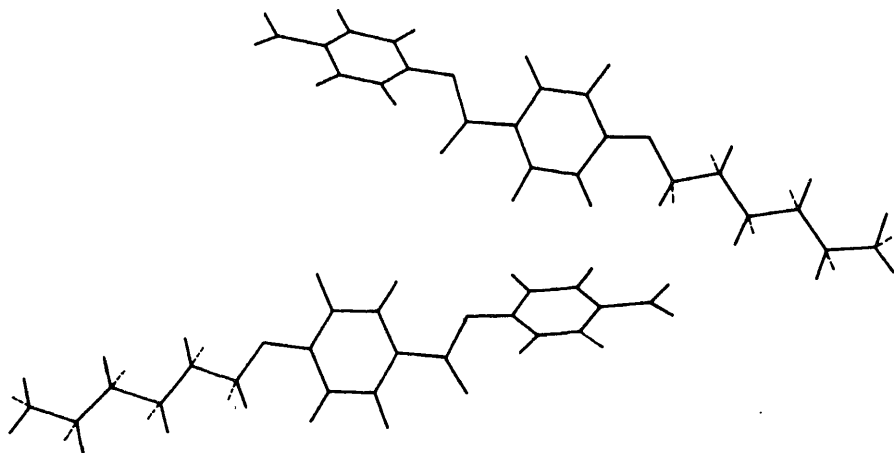


Figure 3. Lowest energy configuration of two NPHB molecules during in-plane interactions

Table 3. Stacking and in-plane interaction energy values between a pair of NPHB molecules (energy in kcal/mole).

Energy terms	Stacking energy	In-plane energy
E_{QQ}	0.40	-0.59
E_{QMI}	0.00	-0.33
E_{MIMI}	-0.33	-0.24
$E_1 (= E_{QQ} + E_{QMI} + E_{MIMI})$	0.07	-1.16
E_{POL}	-0.75	-0.79
E_{DISP}	-19.96	-8.17
$E_2 (= E_{POL} + E_{DISP})$	-20.70	-8.96
E_{REP}	8.38	3.61
$E_{TOT} (= E_1 + E_2 + E_{REP})$	-12.25	-6.51

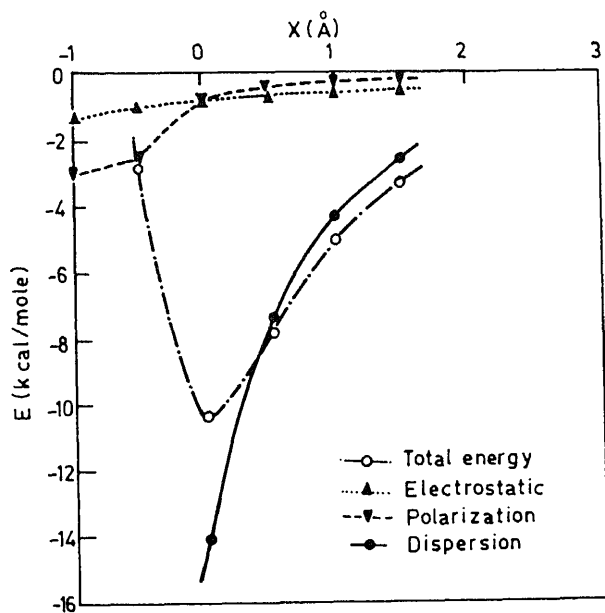


Figure 4. Variation of stacking energy values with intermolecular separation (X). Various components have been plotted corresponding to increasing (+ve) and decreasing (-ve) intermolecular separation with reference to equilibrium point (0) which corresponds to 4.5 Å.

other. The energy for this configuration is -12.25 kcal/mole which is mainly due to dispersive forces (table 3). Figure 4 shows the variations of stacking energy values with respect to intermolecular separation. Since the stacked complex of NPHB molecules selects its minimum energy value at an intermolecular separation of 4.50 Å, this point has been chosen as the reference point and the deviations have been marked as the positive and negative values of intermolecular separation.

separation from the reference point corresponding to minimum energy configuration while the negative sign represents the decreasing separation. It is clear that as the intermolecular separations are increased from the equilibrium value, polarization and electrostatic energies maintain more or less constant values but the contribution of these forces are very small. The total stacking energy curve shows that the energy decreases with inter-molecular separation upto the equilibrium position but on lowering the separation it suddenly increases and ultimately becomes repulsive. A deep and sharp minimum is obtained in the energy curve corresponding to the equilibrium position and the interaction energy for this position has been further recalculated using further refinement. A careful look at the dispersion energy curve suggests that as the overlapping of the molecules increases, the energy always decreases but beyond equilibrium, the repulsive energy which arises due to short range interactions becomes so high that it leads to an increase in the total energy. Hence, it may be inferred that the stacking interactions which play a major role in mesomorphic stability, are mainly due to dispersion forces. Figure 3 shows the in-plane lateral interaction energy configuration where one molecule has been rotated by 180° about its long axis and then translated along an axis perpendicular to the long molecular axis. This corresponds to the lowest energy configuration among all the possible in-plane lateral interaction energy configurations. The corresponding energy is -6.51 kcal/mole which is also mainly due to dispersion forces as observed in the stacking interactions. These configurations are in agreement with those obtained from crystallographic studies. Since NPHB molecules are associated with two highly polar groups ($O16 = -0.352e$ and $O17 = -0.321e$) at one end and a long alkoxychain at the other; terminal (end to end) attractions seem to be improbable due to the non-availability of any proton preventing the formation of any conventional bond. Hence, the present calculations have been restricted to stacking and in-plane interactions. It may be noted that the in-plane lateral energy corresponds to -6.51 kcal/mole which is comparable with the stacking energy (-12.25 kcal/mole) but is higher in comparison with those of other pure nematic liquid crystals (Sanyal *et al* 1984, 1985).

The interaction energy calculations for all the possible configurations show that in closed packed structures, dispersion forces play a key role in stabilizing both the stacking and in-plane lateral interactions as observed in several other cases (Mishra and Tyagi 1973; Baran and Les 1979).

4. Conclusion

It may be concluded, therefore, that inter-molecular interaction energy studies are helpful in understanding the role of molecular forces in accounting for the mesomorphism.

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Determination of stability constants from diffusion coefficient data

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Abstract. Employing diffusion coefficient data evaluated by improved polarographic techniques, stability constants of Cd^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} with biochemical and chemical ligands using 0.1 M NaClO_4 as supporting electrolyte were determined. The range of β values with biochemical ligands were higher than with chemical ligands. A similar trend of high and low β values was established using the Tanaka plot and Bjerrum's method. Thermodynamic parameters reveal no chelate formation with either biochemical or chemical ligands.

Keywords. Stability constant; diffusion coefficient; formation function; polarography.

1. Introduction

The method of Kacena and Matousek (1953) based on diffusion coefficient data for evaluating stability constants of metal complexes had rarely been applied despite its versatility and its advantages, e.g., (i) it is equally applicable to reversible and irreversible electrode processes with a sound theoretical background, (ii) the calculations are much simpler and involve no term which causes error propagation, (iii) variation in i_d ($= D$) are more pronounced as compared to changes in $E_{1/2}$; the latter is, in general, difficult to measure with a fair degree of accuracy and is not required in this method. The technique applicable for 1:1 complexation was employed for Cd-protein interaction by the above authors and its validity was confirmed by Zabransky (1959) for TI-EDTA complexes. The results are comparable with reported data.

The diffusion current was calculated polarographically by simultaneous refinement in $E_{1/2}$ and i_d values evaluated through computerised least-squares method.

The present communication deals with the determination of stability constants of metal ions Zn, Cd, Co and Ni with four ligands—phosphoglyceric acid, phosphoenolpyruvic acid, nitroacetic acid and acetoxyacetic acid. The stability constants were compared with the values obtained separately through the Tanaka plot (Tanaka *et al* 1966) as well as by Bjerrum's method (1941). The thermodynamic parameters (Gupta and Raina 1984), particularly the entropy changes, do not favour chelation.

2. Experimental

2.1 Apparatus

An automatic pen recording polarograph (OH-105 Radelkis, Hungary) with a three-electrode circuitry connected in series with a potentiometer (OSAW-India) and a

heavy current) was employed to record polarograms. The DME had the capillary characteristics $m^{2/3} + t^{1/6} = 2.09 \text{ mg}^{2/3} \text{ s}^{-1/2}$ in 0.1 M NaClO_4 when short circuited. The measurements were made at damping 2, sensitivity $1 \times 10^{-7} \mu\text{A}$ scale division⁻¹, chart speed 2 cm/min, $h = 42$ cm. All the potentials were measured against SCE.

2.2 Chemicals

Phosphoglyceric acid and phosphoenolpyruvic acid (Merck, reagent grade) nitroacetic acid, acetoxyacetic acid and NaClO_4 (SD—AR, purity 99.1–99.5 %) were used without further purification. Metal salts were BDH, AnalaR.

2.3 Procedure

A polarographic cell with a three-electrode system was employed for measuring current–voltage curves. 10.0 ml of the solution P_1 (1 mM metal ion + 0.1 M NaClO_4) was measured accurately and placed in the cell and the other solution P_2 (P_1 + ligand) was introduced to P_1 from the microburette. 0.002 % Triton X-100 was used as suppressor as and when required.

3. Results and discussion

The diffusion controlled reducing nature of metals was established from (i) i_d vs C (ii) i_d vs $h^{1/2}$ and (iii) low temperature coefficient $1.44\text{--}1.49\% \text{ deg}^{-1}$ (25 to 40°). The log plots reveal that Zn^{2+} and Cd^{2+} are reduced reversibly while the irreversible nature of the reduction of Co^{2+} and Ni^{2+} was established. The pre-requisites of the present technique are the diffusion controlled reduction and the general applicability of the Ilkovic equation, hence, the reversible or irreversible nature of the electrode process does not affect the calculations. A single complex formation was clearly evident in all cases from the straight line obtained by the $\log C_L$ vs $E_{1/2}$ plots.

A Hi-basic digital computer spectrum (7/DCM, India) with a provision for 36 k byte words of auxillary memory was employed for simultaneous refinement of graphical i_d and $E_{1/2}$ values through the least-squares method (Gupta and Raina 1984). The data on $E_{1/2}$ and i_d resulted in slope values of $29.5 \pm 0.4 \text{ mV}$ and $29.5 \pm 1.0 \text{ mV}$ in the case of Cd and Zn respectively, thereby justifying the introduction of the improvements given above.

The modified Ilkovic equation due to Koutecky (1953) was used for calculating diffusion coefficients of metal ions (D_M) and metal complexes (D_{ML}). The following equation has been employed to evaluate β_{ML} ,

$$\bar{D}_{\text{app}} = (D_M + D_{ML}\beta_{ML}(L))/(1 + \beta_{ML}(L)), \quad (1)$$

where (L) is the free ligand concentration, $\bar{D}_{\text{app}}$ (the apparent diffusion coefficient corresponding to the total wave height for the simultaneous reduction of M and ML in the mixture), D_M and D_{ML} are the diffusion coefficients of M ions and the ML complex respectively. The limiting value of i_d obtained with the increasing amount of ligand was considered as i_{dML} . By carefully adjusting the ligand concentration, the appropriate condition $i_d = i_{dML}$ (minimum) was set up. The free ligand concentration (L) was

calculated by the straightforward methods reviewed by Leggett (1982). Table 1 reveals the ligand concentrations (L) where i_{dML} was minimum. The value has been reported as i_{dML} from which D_{ML} was calculated. The average of D_M and D_{ML} is $\bar{D}_{app}$, which subsequently gave β_{ML} . The free and total ligand and metal ion concentrations were used for calculating the Bjerrum function, $\bar{n}$ which in turn provides the stability constant as the intercept on the ordinate from the following equation

$$\bar{n}/(1 - \bar{n})(L) = \beta_1 + \{[(2 - \bar{n})/(1 - \bar{n})](L)\beta_2\}. \quad (2)$$

Table 2 lists the Bjerrum function, $\bar{n}$, and other parameters for evaluating β_1 for certain representative systems, while β_1 for all the systems studied are shown in table 1.

The stability constants were recalculated by using the total ligand concentration using the equation of Tanaka *et al* (1966). Figure 1 shows the variation of $(C_L/(D_M - \bar{D}_{app}))$ with increasing amounts of C_L (the total ligand concentration), the slope and intercept of which result in β_{ML} .

$$C_L/(D_M - \bar{D}_{app}) = (1 + \beta_{ML}C_L)/\{\beta_{ML} + (D_M - \bar{D}_{ML})\} \quad (3)$$

The β_{ML} values obtained by this method, presented in table 1 fall within 10% of the values resulting from the former two techniques. The contribution of the supporting electrolyte NaClO_4 in promoting or inhibiting complexation is minimum as reported by Beck (1977).

The validity of the set of stability constants calculated by the present method is tested by determining the precision i.e. the average deviation from the mean values (vide table 1). It is evident that the smaller the deviation, the better the corresponding fit. But the inspection of data in this case could not help in deciding which method is better. Preference is given to one developed by Kacena and Matousek (1953) because it describes the process with a lesser number of parameters.

ΔF , ΔH and ΔS have been determined from the following equations

$$\Delta F = -2.303 RT \log \beta_1, \quad (4)$$

$$\Delta H = (-4.576 T_1 T_2 \Delta \log \beta_1)/(T_2 - T_1) \quad (5)$$

and

$$\Delta S = (\Delta H - \Delta F)/T \quad (6)$$

ΔH was also obtained graphically from the slope of the plot $\log \beta_1$ vs $1/T$. The thermodynamic quantities thus calculated on the basis of β values are presented in table 3. As could be seen from the data summarised in the table, the absolute values of ΔF , ΔH and ΔS remain constant for a particular system. The entropy values are lower, in general, for the ligands nitroacetic acid and acetoxyacetic acid, irrespective of the metal ion, as compared with the other two ligands (the highest being in the case of Co-phosphoenolpyruvic acid); however, the observations of Spike and Parry (1953) indicate that the trend of values do not really favour chelate formation.

In the case of nitroacetic acid and acetoxyacetic acid, the charge neutralization, and consequently, the degree of solvation is comparatively less as compared to phosphoglyceric acid and phosphoenolpyruvic acid. This may induce small changes in solvent orientation and invariably lowers the ΔS , and is thus expected to disfavour the reaction. Low values of β can thus be anticipated.

The ligands, substituted monocarboxylic acid derivatives of acetic acid and

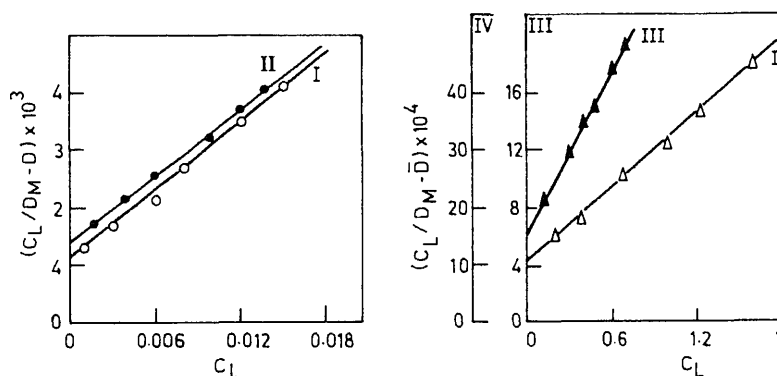
Table 1. Complexes of ligands with metals.

Ligand*	(L)	i_{ML}	$D_{ML} \times 10^{-6}$	$\bar{D}_{app} \times 10^{-6}$	β_{ML}	β (Bjerrum)	β (Tanaka)	β (Mean)	Average deviation from mean	β reported (Martell and Smith 1977)
Zn²⁺, $i_d = 7.33 \mu A$, $D_M = 8.345 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$										
PGA	0.0095	1.849	0.531	4.438	105.3	105	111.0	107.1	2.6	2512
PPA	0.0076	1.980	0.608	4.476	131.5	130	133.2	131.5	1.1	912
NAA	0.933	2.565	1.022	4.683	1.07	1.0	1.03	1.03	0.02	1.07
AAA	0.215	2.402	0.896	4.620	4.65	4.5	4.0	4.38	0.26	4.3
Cd²⁺, $i_d = 7.329 \mu A$, $D_M = 8.345 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$										
PGA	0.009	4.031	2.524	5.435	118.6	120	120.0	119.5	0.6	2512
PPA	0.012	1.832	0.521	4.433	80.0	80	77.2	79.0	1.3	912
NAA	0.670	2.345	0.854	4.599	1.5	2.0	2.3	1.8	0.3	1.55
AAA	0.080	2.200	0.751	4.548	12.34	12.5	14.3	13.0	0.8	12.6
Co²⁺, $i_d = 7.153 \mu A$, $D_M = 7.95 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$										
PGA	0.0075	1.907	0.565	4.257	133.3	135	141.2	136.5	3.46	933
PPA	0.0055	1.920	0.573	4.262	173.1	180	181.8	178.3	3.13	346
NAA	0.891	2.346	0.855	4.403	1.122	1.2	1.93	1.42	0.34	1.0
AAA	0.40	2.20	0.752	4.351	2.43	2.5	3.15	2.36	0.33	2.45
Ni²⁺, $i_d = 7.176 \mu A$, $D_M = 8.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$										
PGA	0.0083	1.865	0.540	4.270	120.7	120	119.6	120.1	0.40	758
PPA	0.055	2.008	0.626	4.313	178.7	18.0	20.20	18.7	0.43	219
NAA	0.880	2.510	0.9795	4.489	1.137	1.2	1.57	1.3	0.18	1.15
AAA	0.225	2.534	0.7196	4.35	4.448	4.5	5.93	4.96	0.65	4.26

* PGA = phosphoglyceric acid; PPA = phosphoenolpyruvic acid; NAA = nitroacetic acid; AAA = acetoxyacetic acid.

Table 2. Bjerrum function $\bar{n}$ and data for calculating β_1 .

C_L	(L)	$\bar{n}$	$[\bar{n}/(1 - \bar{n})(L)]$	$[(2 - \bar{n})(L)/(1 - \bar{n})]$
<i>Zn-phosphoenolpyruvic acid</i>				
0.0052	0.0046	0.60	326	0.016
0.00632	0.0056	0.72	459	0.025
0.00746	0.0066	0.86	930	0.054
0.00852	0.0076	0.92	1513	0.102
<i>Cd-acetoxycetic acid</i>				
0.0505	0.05	0.52	21.66	0.154
0.0607	0.06	0.68	35.41	0.247
0.0708	0.07	0.85	80	0.536
0.0809	0.08	0.92	144	1.080
<i>Co-phosphoglyceric acid</i>				
0.0051	0.0045	0.60	333	0.016
0.00623	0.0055	0.73	491	0.026
0.00735	0.0065	0.85	871	0.050
0.00845	0.0075	0.95	2533	0.157
<i>Ni-nitroacetic acid</i>				
0.50061	0.50	0.61	3.13	1.78
0.64076	0.64	0.76	4.94	3.30
0.75087	0.75	0.87	8.92	6.51
0.88097	0.88	0.97	36.70	30.21

**Figure 1.** Variation of $[C_L / (D_M - \bar{D}_{app})]$ for Co^{2+} with the total ligand concentration I phosphoenolpyruvic acid II phosphoglyceric acid III acetoxycetic acid IV nitroacetic acid

oxygen atom of the carboxylate moiety or the oxygen atom of the substituent group. It could be inferred from low and high β values that the coordination of the donor atom in case of chemical ligands is different from that of biochemical ligands (in the absence of the chelating effect). In the latter case, the linkage is decidedly through the O atom of a considerably hard base (Ahrlund *et al* 1958) of the phosphate group, while the carboxylate moiety is preferentially attached in case of nitroacetic acid and acetoxycetic acid to give relatively low β values.

Table 3. Calculated thermodynamic quantities.

<i>T</i> (°C)	β_1	$-\Delta F$ (kcal/mole)	$-\Delta H$ (kcal/mole) calculated	From graph	$-\Delta S$ (cal/deg/mole)
<i>Cd-phosphoglyceric acid</i>					
25	118.6	2.828	—	4.41	5.30
30	106.8	2.812	3.77	4.41	5.27
35	95.0	2.786	4.33	4.41	5.27
<i>Cd-phosphoenolpyruvic acid</i>					
25	80.0	2.595	—	4.46	6.26
30	72.1	2.576	3.73	4.46	6.21
35	63.9	2.544	4.47	4.46	6.22
<i>Cd-nitroacetic acid</i>					
25	1.50	0.240	—	4.43	14.06
30	1.35	0.181	3.78	4.43	14.03
35	1.20	0.111	4.36	4.43	14.02
<i>Cd-acetoxyacetic acid</i>					
25	12.34	1.487	—	4.99	11.76
30	11.04	1.446	3.99	4.99	11.70
35	9.60	1.384	5.18	4.99	11.70
<i>Zn-phosphoglyceric acid</i>					
25	105.30	2.758	—	4.42	5.58
30	94.77	2.740	3.78	4.42	5.54
35	84.30	2.714	4.33	4.42	5.53
<i>Zn-phosphoenolpyruvic acid</i>					
25	131.5	2.889	—	4.44	5.20
30	118.3	2.879	3.80	4.44	5.17
35	105.2	2.849	4.35	4.44	5.16
<i>Zn-nitroacetic acid</i>					
25	1.07	0.040	—	1.15	3.72
30	1.04	0.023	1.02	1.15	3.72
35	1.01	0.006	1.08	1.15	3.71
<i>Zn-acetoxyacetic acid</i>					
25	4.65	0.911	—	4.44	11.84
30	4.19	0.862	3.80	4.44	11.81
35	3.72	0.805	4.36	4.44	11.80
<i>Co-phosphoglyceric acid</i>					
25	133.3	2.897	—	4.18	4.30
30	120.9	2.887	3.51	4.18	4.27
35	108.0	2.866	4.18	4.18	4.26
<i>Co-phosphoenolpyruvic acid</i>					
25	173.1	3.052	—	3.80	2.51
30	156.8	3.039	3.78	3.80	2.51
35	143.0	3.037	3.17	3.80	2.47
<i>Co-nitroacetic acid</i>					
25	1.12	0.067	—	1.66	5.35
30	1.08	0.046	1.31	1.66	5.33
35	1.03	0.018	1.76	1.66	5.33
<i>Co-acetoxyacetic acid</i>					
25	2.43	0.526	—	3.77	10.88
30	2.20	0.475	3.57	3.77	10.87
35	2.01	0.427	3.35	3.77	10.85
<i>Ni-phosphoglyceric acid</i>					
25	120.7	2.839	—	4.39	5.20

Table 3. (Continued)

<i>T</i> (°C)	β_1	$-\Delta F$ (kcal/mole)	$-\Delta H$ (kcal/mole) calculated	From graph	$-\Delta S$ (cal/deg/mole)
<i>Ni-phosphoenolpyruvic acid</i>					
25	17.9	1.708	—	4.46	9.23
30	16.1	1.673	3.81	4.46	9.19
35	14.3	1.628	4.40	4.46	9.19
<i>Ni-nitroacetic acid</i>					
25	1.14	0.078	—	1.83	5.88
30	1.09	0.051	1.61	1.83	5.87
35	1.04	0.024	1.74	1.83	5.86
<i>Ni-acetoxyacetic acid</i>					
25	4.45	0.884	—	4.27	11.36
30	4.02	0.837	3.65	4.27	11.33
35	3.59	0.782	4.19	4.27	11.32

depict the major driving force for the charge neutralization process causing the complexation. Jones *et al* (1958) and Clarke *et al* (1963) approved the relationship connected with the basic strength of the ligand and the log of the stability constant by interpreting the π -electron interactions of the metal ligand bond. However, the electron density at the basic centre of the biochemical ligands would almost be the same due to P–O groupings, hence, the stability constants will also be nearly equal. The same would be the case with chemical ligands having C–O bonds. Thus the similarity of β values between the sets of biochemical and chemical ligands is certain and is clearly evident from the observation made herein (vide table 1).

Wold and Ballou (1957) during the interconversion study of 2-glyceric acid 2-phosphate and enolpyruvic acid phosphate attempted to derive an expression containing variations of apparent equilibrium constant with pH and metal concentration. The calculations are deprived of the true equilibrium rigour and hence the validity of data is rather doubtful, subsequently the reported high β values with phosphoglyceric and phosphoenolpyruvic acids (vide the last column of table 1) cannot be considered worth comparing. However, the β values with acetoxyacetic acid and nitroacetic acid are highly comparable e.g., Co-acetoxyacetic acid—reported 2.45, this work 2.43; Cd-nitroacetic acid—reported 1.55, this work 1.5; Zn-nitroacetic acid—reported 1.07, this work 1.07 and so on (table 1).

It can be concluded that the interaction of metal ions with biochemical ligands results in stronger complexes than with chemical ligands.

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Magnetic and spectral studies on 3d-metal complexes of acetone(N-isopropylidene)tyrosyl hydrazone

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Abstract. Acetone(N-isopropylidene)tyrosyl hydrazone, $\text{HO-C}_6\text{H}_4\text{-CH}_2\text{-CH(N=CMe}_2\text{)-CONHN=CMe}_2$ (ATH), has been found to form adducts of the type $M(\text{ATH})\text{Cl}_2 \cdot n\text{H}_2\text{O}$ [$M = \text{Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)}$; $n = 0, 1$ or 2] and deprotonated complexes of the type $M'(\text{ATH-2H}) \cdot 3\text{H}_2\text{O}$ [$M' = \text{Co(II), Ni(II) and Cu(II)}$]. Molar conductance studies in 0.001 M DMSO solution have indicated the non-ionic nature of the complexes. High-spin octahedral geometry for Mn(II) and Ni(II) complexes and tetrahedral geometry for Co(II) adduct have been proposed on the basis of magnetic and/or electronic spectral studies. IR spectra suggest neutral bidentate and dinegative tridentate behaviour of the ligand in the adducts and deprotonated complexes respectively. ESR spectra of Cu(II) complexes indicate zero-field splitting of $\text{Cu(ATH)Cl}_2 \cdot \text{H}_2\text{O}$ and metal-metal interaction in both the complexes.

Keywords. Acetone(N-isopropylidene)tyrosyl hydrazone; 3d-metal complexes; deprotonated complexes; neutral bidentate behaviour; dinegative tridentate behaviour.

1. Introduction

In view of a current upsurge of interest in the transition metal complexes of biologically active ligands, particularly of amino acids and their derivatives (McAuliffe and Murray 1973; Bunel *et al* 1981; Bontchev *et al* 1981; Antolini *et al* 1982), we recently initiated in this laboratory an investigation on the coordination properties of amino acid hydrazides and their derivatives; in this frame work we have previously reported the synthesis and structural studies of first row transition metal complexes of 1-tyrosine hydrazide and (N-benzoyl)glycine hydrazide (Rao *et al* 1984; Rao *et al* 1985).

In the present paper we describe the results of our investigations on the synthesis and structural studies of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of acetone(N-isopropylidene)tyrosyl hydrazone (ATH).

2. Experimental

2.1 Starting materials

All the metal chlorides used in this study were of BDH, AR grade. 1-Tyrosine hydrazide, obtained from M/s Sigma Chemical Company, USA, was used as such. Acetone(N-isopropylidene)tyrosyl hydrazone was prepared by refluxing 1-tyrosine hydrazide in

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the reaction mixture to room temperature was separated by filtration, washed with acetone and ether and recrystallized from acetone, m.p. 145°C. Analysis: calcd. for $C_{15}H_{21}N_3O_2$: C, 65.47; H, 7.63; N, 15.26; N_2H_4 , 11.63%. Found: C, 65.23; H, 7.59; N, 15.20; N_2H_4 , 11.58%.

2.2 Preparation of the complexes

Complexes of the general formula $M(ATH)Cl_2 \cdot nH_2O$ [$M = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$] were prepared by adding a solution of ≈ 2.5 mmol of ATH in acetone to a solution of the appropriate metal chloride (≈ 2.5 mmol) in an acetone-ethanol mixed solvent. Addition of a few drops of dil. HCl to the above metal-ligand solution resulted in the formation of a gummy solid in each case, which on maceration with acetonitrile, yielded the micro-crystalline complex. The complexes, thus obtained, were filtered, washed with acetone and ether and dried in a desiccator.

Complexes of the general formula $M'(ATH-2H) \cdot 3H_2O$ [$M' = Co(II), Ni(II)$ and $Cu(II)$] were synthesized as follows: To an aqueous solution of ATH ammonium hydroxide was added drop by drop until its pH rose to ≈ 6.5 followed by the addition of an aqueous solution of the appropriate metal chloride in equimolar ratio. The complexes precipitated immediately and were digested on a water bath for ≈ 5 min, filtered, washed successively with water, ethanol and ether and dried at room temperature.

2.3 Analyses of the complexes

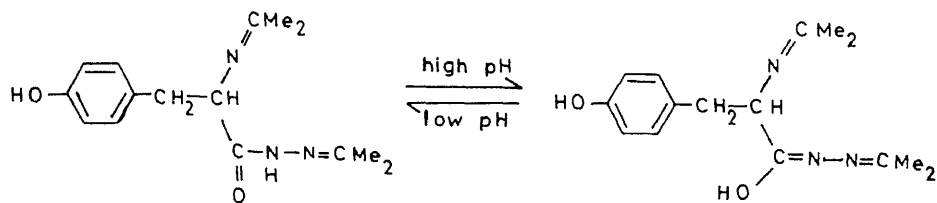
The metal and the halide were analysed gravimetrically. Hydrazine was estimated volumetrically after subjecting the complexes to acid hydrolysis. The water content of the complexes was determined from the loss of weight suffered by them on heating in the temperature range 90–200°C. C, H and N were microanalysed. The analytical data are given in table 1.

2.4 Physical measurements

Details of the equipment used for various physico-chemical studies were the same as reported earlier (Rao *et al* 1984; Rao *et al* 1985). Effective magnetic moments are included in table 1 while the spectral data are given in tables 2 and 3.

3. Results and discussion

The analytical data in table 1 show that the metal-ligand interaction gives rise to the formation of two types of complexes, viz, the adducts and the neutral or deprotonated complexes in weakly acidic and alkaline media respectively. Based on the formation of the deprotonated complexes, an amide $\rightleftharpoons$ imidol tautomerism of α -amino acid function of



pH may be formulated as shown above: It appears from the dinegative behaviour of the ligand in the neutral complexes that besides the deprotonation of the imidol group, elimination of the phenolic proton also occurs as that reported for tyrosine (Chow and McAuliffe 1975).

The complexes are non-hygroscopic and fairly stable under ordinary atmospheric conditions. With a few exceptions all of them are insoluble in water and common organic solvents but are soluble in DMF and DMSO. All the adducts are found to melt at specific temperatures as given in table 1 while the deprotonated complexes are non-melting below 300°C. The insolubility in common organic solvents and the non-melting nature of the deprotonated complexes suggest a polymeric nature. The molar conductance values of the complexes in 0.001 M DMSO solutions lie in the range 0.47–7.1 ohm⁻¹ cm² mol⁻¹ indicating their non-ionic nature (Geary 1971).

3.1 Magnetic moments

The room temperature magnetic moments indicate a spin-free tetrahedral or octahedral geometry for the Mn(II) complex and octahedral geometry for Ni(II) complexes (Figgis and Lewis 1964). The μ_{eff} value obtained for Co(ATH)Cl₂ is typical of a tetrahedral stereochemistry (Figgis and Lewis 1964) while the subnormal magnetic moment (3.23 BM) of Co(ATH-2H)·3H₂O may be explained by assuming a polymeric formulation with magnetic exchange (Williams *et al* 1967; Henke and Kremer 1982). The magnetic moments of Cu(II) complexes which are slightly lower than the spin-only value, reflect the presence of a weak metal-metal interaction (Kato *et al* 1964).

3.2 Electronic spectra

The electronic spectra of the complexes have been recorded as nujol mull; the band maxima, their assignments and the calculated ligand-field parameters are given in table 2. The data indicate a tetrahedral geometry for Co(ATH)Cl₂ (Cotton *et al* 1961) and an octahedral environment around Ni(II) in its complexes (Lever 1968). The band positions of Cu(II) complexes suggest a pseudo-octahedral geometry (Lever 1968). These assignments are in accord with the conclusions drawn earlier based on the room temperature magnetic moments of the complexes.

Table 1. Elemental analysis and general behaviour of ATH complexes.

Complex	Colour	Nature	M.P. (°C)	Analysis found (calcd.) %							μ_{eff} (B.M)
				M	C	H	N	Cl	N ₂ H ₄		
Mn(ATH)Cl ₂ · 2H ₂ O	Light yellow	Microcrystalline	195	12.60 (12.57)	41.04 (41.20)	5.67 (5.72)	9.54 (9.61)	16.44 (16.32)	7.48 (7.32)	6.15	
Co(ATH)Cl ₂	Blue	Microcrystalline	180	14.48 (14.55)	44.31 (44.46)	5.22 (5.18)	10.26 (10.37)	17.31 (17.51)	7.88 (7.90)	4.30	
Ni(ATH)Cl ₂ · 2H ₂ O	Green	Microcrystalline	277 ^d	13.31 (13.32)	40.72 (40.85)	5.62 (5.67)	9.48 (9.53)	16.14 (16.09)	7.27 (7.26)	2.80	
Cu(ATH)Cl ₂ · H ₂ O	Green	Microcrystalline	148	14.78 (14.87)	42.04 (42.10)	5.43 (5.38)	9.77 (9.82)	16.48 (16.59)	—	1.63	
Zn(ATH)Cl ₂ · 2H ₂ O	Yellow	Microcrystalline	240	14.66 (14.62)	40.30 (40.24)	5.39 (5.59)	9.28 (9.39)	15.63 (15.85)	7.40 (7.15)	Dia- mag.	
Co(ATH-2H) · 3H ₂ O	Brown	Noncrystalline	> 300	15.21 (15.27)	46.61 (46.64)	6.51 (6.48)	10.86 (10.88)	—	8.42 (8.29)	3.23	
Ni(ATH-2H) · 3H ₂ O	Light pink	Noncrystalline	> 300	15.29 (15.22)	46.72 (46.67)	6.40 (6.48)	10.72 (10.88)	—	8.58 (8.30)	2.76	
Cu(ATH-2H) · 3H ₂ O	Blue	Noncrystalline	185 ^d	16.17 (16.27)	46.11 (46.08)	6.31 (6.40)	10.77 (10.75)	—	—	1.54	

^d Decomposition temperature.

Table 2. Electronic spectral data and various ligand-field parameters of ATH complexes.

Complex	Band maxima (cm ⁻¹)	Assignments	Dq (cm ⁻¹)	B' (cm ⁻¹)	β (%)	LFSE (kJ/mole)
Co(ATH)Cl ₂	6250, 15380	$^4A_2 \rightarrow ^4T_1(F), ^4T_1(P)$	360	721	0.75	52
Ni(ATH)Cl ₂ · 2H ₂ O	9091, 13990, 22220	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F), ^3T_{1g}(F), ^3T_{1g}(P)$	909	596	0.56	130
Cu(ATH)Cl ₂ · H ₂ O	15270	$^2E_g \rightarrow ^2T_{2g}$	1527	—	—	109
Co(ATH-2H) · 3H ₂ O	8335, 16000	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F), ^4T_{1g}(P)$	922	577	0.60	88
Ni(ATH-2H) · 3H ₂ O	10150, 15620, 19050	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F), ^3T_{1g}(F), ^3T_{1g}(P)$	1015	634	0.60	146
Cu(ATH-2H) · 3H ₂ O	15500	$^2E_g \rightarrow ^2T_{2g}$	1550	—	—	110

Table 3. ESR parameters of copper complexes of ATH.

Complex	g_{iso}	$g_{\parallel}$	$g_{\perp}$	A_{iso}^a	$A_{\parallel}^a$	$A_{\perp}^a$	G	$D_{\parallel}$ (gauss)
$\text{Cu(ATH)Cl}_2 \cdot \text{H}_2\text{O}$	2.129	2.241	2.072	50.66	113.6	19.16	3.34	40.0
$\text{Cu(ATH-2H)} \cdot 3\text{H}_2\text{O}$	2.122	2.242	2.062	72.68	168.2	24.91	3.90	—

^a Units, $\times 10^{-4} \text{ cm}^{-1}$.

(Goodman and Raynor 1970). An elongated tetragonal-octahedral stereochemistry is proposed for both the complexes in consistence with their lowest g values greater than 2.04 (Bertini *et al* 1979). The identical $g_{\parallel}$ values observed for the complexes indicate a similar type of bonding arising from a CuNO_3 chromophore in each of the complexes Massaccesi *et al* 1978 & 1979).

The spectrum of $\text{Cu(ATH)Cl}_2 \cdot \text{H}_2\text{O}$ seems to be more complicated due to the presence of zero-field splitting appropriate for a triplet state. Both the overlapping seven-line sets have been identified in the parallel region of the DMF-glass spectrum and its analysis gives $D_{\parallel} \approx 40\text{G}$. Besides, as a consequence of the exchange interaction, the $A_{\parallel}$ value comes to be $113.6 \times 10^{-4} \text{ cm}^{-1}$ which is almost half of that for $S = 1/2$ species (Hasty *et al* 1978). The presence of significant exchange interaction in these complexes is also indicated by the fact that $G < 4.0$ (Hathaway and Billing 1970), where $G = g_{\parallel} - 2)/(g_{\perp} - 2)$. Further, the spectra show intense peaks centered at 1610 G ($g = 3.98$) and 1700 G ($g = 3.82$) in the $\Delta M_s = 2$ region of the $\text{Cu(ATH)Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Cu(ATH-2H)} \cdot 3\text{H}_2\text{O}$ respectively suggesting the presence of metal-metal interaction (Smith and Pilbrow 1974).

3.4 Infrared spectra

The bonding sites of ATH involved in the adducts as well as the neutral complexes have been determined by a careful comparison of the IR spectra of the complexes with the spectrum of the ligand. ATH shows a band at 1670 cm^{-1} in the solid state and at 1690 cm^{-1} in acetonitrile solution due to $>\text{C}=\text{O}$ stretching frequency indicating the involvement of the $>\text{C}=\text{O}$ group in hydrogen bonding in the solid state. To minimise the effect of hydrogen bonding, the spectra of the complexes have been compared with the solution spectrum of the ligand. As the spectra of the complexes in the NH stretching region are very complicated due to the overlap of $\nu(\text{NH})$ and $\nu(\text{OH})$ absorptions resulting into a broad band, we have refrained from drawing any conclusion from the bands appearing in this region. The bands arising in the solution spectrum of the ligand at 1690, 1610, 1510, 1320 and 1035 cm^{-1} are assigned to amide I, $\nu(\text{C}=\text{N})$, amide II, amide III and $\nu(\text{N}-\text{N})$ modes respectively (Nagano *et al* 1964); the corresponding bands in the spectra of the adducts are observed in the 1665–1625, 1600–1590, 1490–1480, 1340–1335 and $1090\text{--}1080 \text{ cm}^{-1}$ regions. Thus, a negative shift in the amide I and amide II bands and a positive shift in the amide III band observed in the spectra of the adducts indicate bonding through the oxygen of the amide group (Nagano *et al* 1964). However, the absence of amide I, II and III bands and the presence

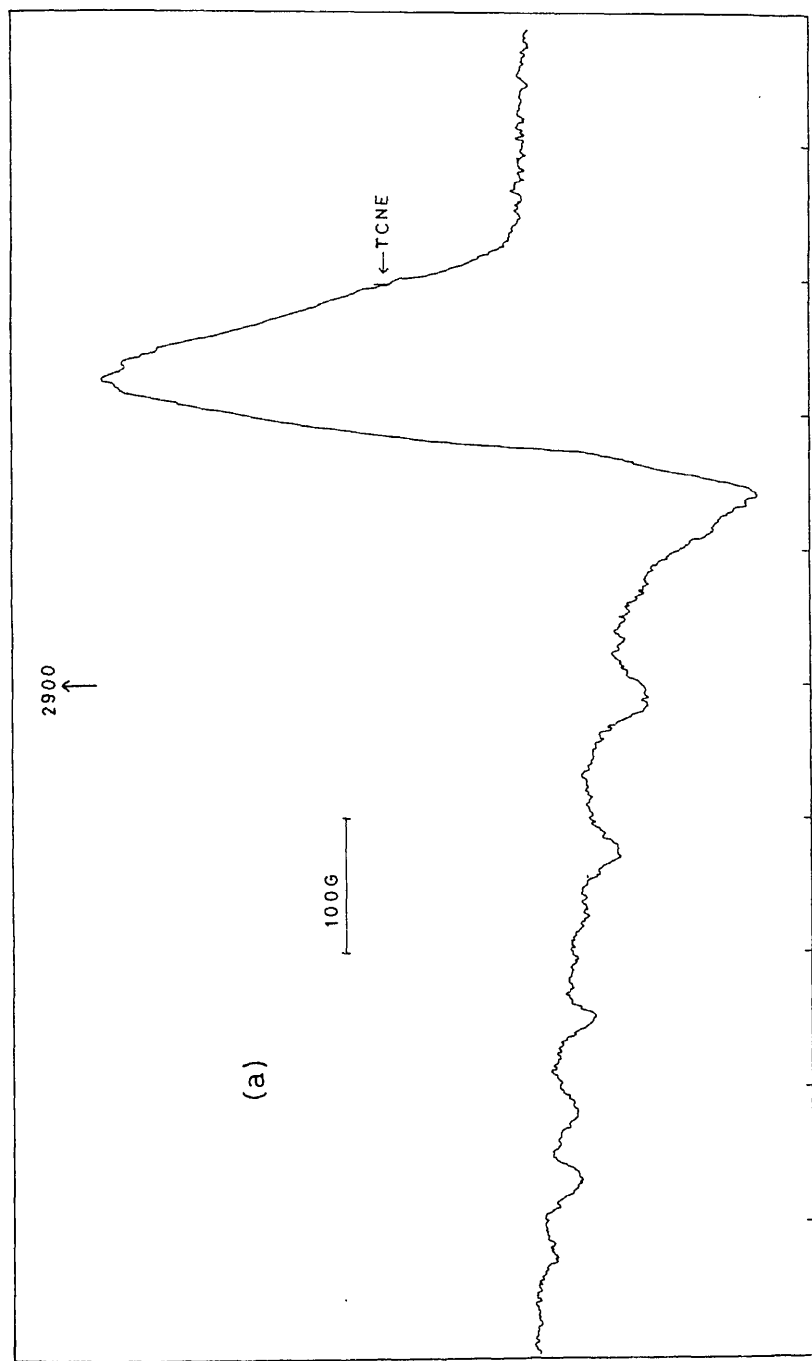


Figure 1. a

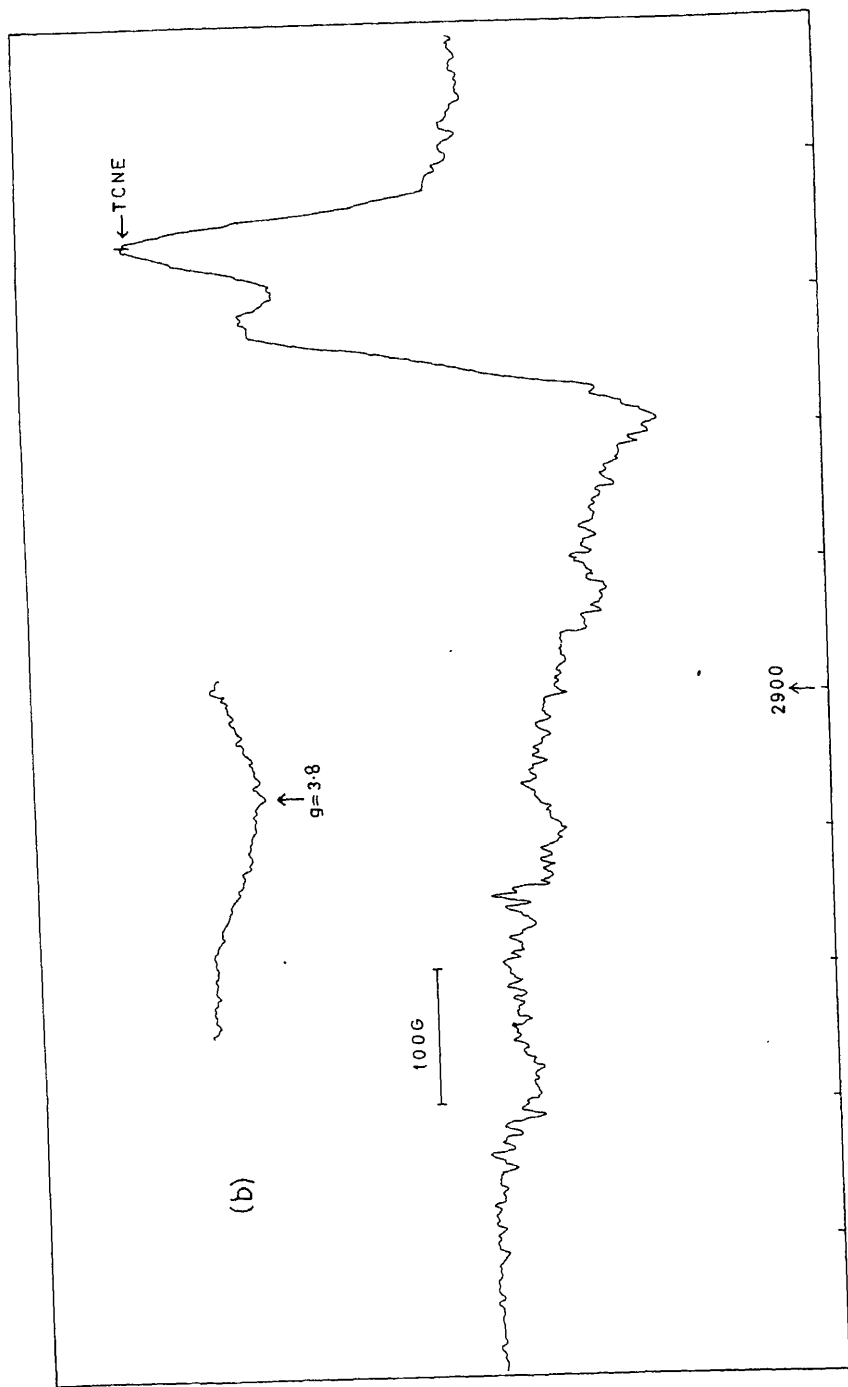


Figure 1. ESR spectrum of **a.** $\text{Cu(ATH)Cl}_2 \cdot \text{H}_2\text{O}$, and **b.** $\text{Cu(ATH-2H)} \cdot 3\text{H}_2\text{O}$, in DMF at liquid nitrogen temperature.

in the spectra of the deprotonated complexes show the destruction of the keto group through amide $\rightleftharpoons$ imidol tautomerism (Rao 1963). Further, a negative shift in position of the azomethine group of the hydrazone moiety in the spectra of all complexes compared to that of the ligand indicates coordination through azomethine nitrogen (Rao 1963); coordination through this group is further substantiated by the observed positive shift of the order $50\text{--}60\text{ cm}^{-1}$ in the $\nu(\text{N--N})$ mode in all the complexes (Braibanti *et al* 1968). The bands appearing in the free ligand at 1235 and 620 cm^{-1} assigned to the in-plane and out-of-plane deformation modes of the phenolic-OH group (Inomata *et al* 1974) remain almost unaltered in the spectra of the adducts while both the bands disappear in the deprotonated complexes indicating the non-involvement of the phenolic-OH group in the former complexes and its deprotonation of the same and subsequent coordination in the latter (Inomata *et al* 1974). The non-ligand bands appearing in the $480\text{--}400$ and $340\text{--}290\text{ cm}^{-1}$ region of the spectra of the adducts as well as the neutral complexes may be tentatively assigned to $\nu(\text{M--N})$ and $\nu(\text{M--O})$ modes respectively (Nakamoto 1978).

In order to make more unequivocal assignments of the band positions due to $\nu(\text{M--O})$ and $\nu(\text{M--N})$ modes, far IR spectra of two representative complexes $\text{Cu}(\text{ATH})\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{ATH-2H}) \cdot 3\text{H}_2\text{O}$ were recorded in the region $650\text{--}100\text{ cm}^{-1}$. The spectrum of $\text{Cu}(\text{ATH})\text{Cl}_2 \cdot \text{H}_2\text{O}$ shows two strong peaks at 443 and 326 cm^{-1} while that of $\text{Cu}(\text{ATH-2H}) \cdot 3\text{H}_2\text{O}$ appear at 460 and 340 cm^{-1} ; the former peak in each case may be assigned to $\nu(\text{M--N})$ while the latter to $\nu(\text{M--O})$ mode (Herlinger and Long 1970; Kincaid and Nakamoto 1976).

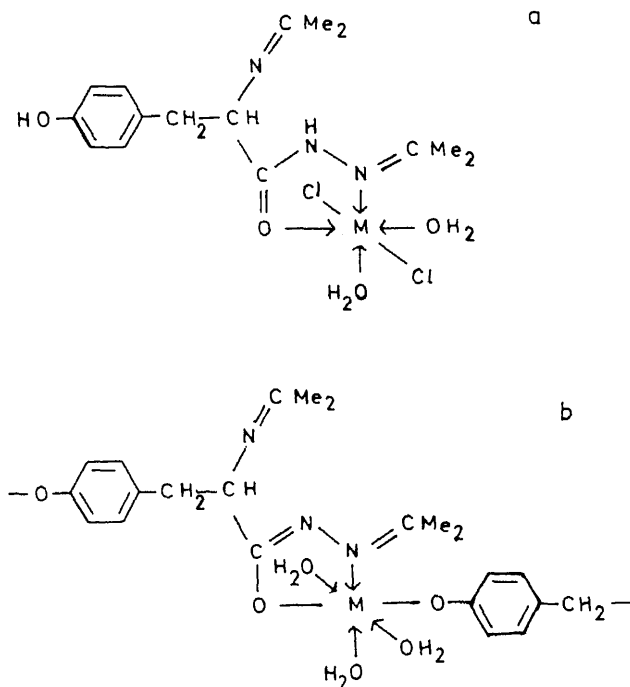


Fig. 2. Structures of (a) $\text{M}(\text{ATH})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (M = Cu, Ni, Zn) and (b) $\text{M}(\text{ATH-2H}) \cdot 3\text{H}_2\text{O}$ (M = Cu, Ni, Zn).

Based on the chemical composition and various physico-chemical studies, structures shown in figure 2a and b may be tentatively proposed for the ATH complexes.

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Syntheses of oxochlorochromates(V)

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Abstract. Syntheses of three stable complexes of Cr(V) have been described which were characterised by elemental analysis, IR, electronic spectral, ESR and magnetic studies. The size and charge of the counter ion determines the overall composition of the Wienland salts. Apparently the isolation of oxotetra-, penta- and hexachlorochromates(V) of benzimidazolium, biquinolinium and terpyridinium cations respectively were achieved. These oxochlorochromates possibly contained the same oxotetrachlorochromate(V) species.

Keywords. Cr(V); oxochlorochromates(V); Wienland salts.

1. Introduction

Our earlier work (Majumder and Mitra 1975; Mitra 1979; Majumder and Saha 1976) on the syntheses of chromium(V) compounds, together with others from the literature, corroborates the general impression of preparative chemists, which has been described as 'inorganic symbiosis' by Jorgenson (1964) and elaborated by Basolo (1968) that ions of similar size, charge and shape usually tend to associate with like ions to produce crystals of good stability. Often this is a useful guide for chemical syntheses. If the counter ions are large and univalent, oxotetrachlorochromates(V) like $M[CrOCl_4]$ (where $M = R_4N$, $R =$ alkyl group, PyH , Ph_4As , Ph_4P etc) are isolated from a solution of Cr^VOCl_3 containing HCl. On the other hand, if the cations are large and bivalent $RH_2[CrOCl_5]$ are isolated (where $R =$ phenanthroline, bipyridine, phenazine etc). With these cues it was decided to study the effects of uni-, bi- and trivalent cations on the overall composition and properties of the oxochlorochromates(V) and hence the following experiments were undertaken.

2. Materials and methods

2.1 Materials

The preparation and/or purification of chromylchloride, acetic acid, benzene, etc. have been described earlier (Majumder and Mukhopadhyay 1973). Benzimidazole was prepared by the condensation of *o*-phenylenediamine with formic acid in alkaline solution. The crude benzimidazole was purified from water and the m.p. found to be 171°C, 2,2'-biquinoline (GR, E. Merck) and 2,2',6',2'' terpyridine (Fluka AG) were used as such.

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2.2 Synthetic outlines

The preparative method used here was a slight modification of the classical method of Meyer and Best (1899) and of Wienland and Friedrerr (1907). We have used pure chromyl chloride in anhydrous acetic acid through which dry HCl gas was passed under cold conditions (0°C). To this reduced chromyl chloride (presumably containing CrOCl_3 plus HCl) the base (also dissolved in acetic acid) was added (actually pumped into the solution in a specially designed all glass apparatus fitted with a filter stick). Filtration was done in the same assembly by tilting the flask out of contact with the atmosphere. The compound was washed with cold purified acetic acid and finally with benzene and left overnight in a vacuum desiccator over conc. H_2SO_4 . The yields were excellent. The methods of analysis have been described earlier (Majumder and Mitra 1975).

2.3 The infrared spectra

The IR spectra were recorded in the KBr phase. The electronic spectra were recorded on a Beckmann DU 2 spectrophotometer at room temperature. Magnetic susceptibilities were measured in a Guoy balance at room temperature (25°C). $\text{HgCo}(\text{SCN})_4$ was used as the calibrant. Calculations and corrections of the magnetic moment values were made according to Figgis and Lewis. The ESR instrument was an X-band spectrometer (at the Saha Institute of Nuclear Physics, Calcutta, through the courtesy of Dr. Asis Roy) operating near 9.44 GHz, using a 100 kHz field modulation. The first derivative ESR spectra were recorded.

3. Results and discussions

Analytical and spectral data are presented in tables 1 and 2, the ESR spectra in figure 1. Conductances of II and III could not be measured due to the non-availability of a suitable solvent. II and III on dissolution in some solvents (e.g. acetonitrile, nitromethane) yielded white precipitates of the hydrochlorides of biquinoline and terpyridine. Molar conductance of I in acetone was found to be $125 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ indicating a 1:1 type of electrolyte.

The substances were apparently magnetically dilute and the IR spectra showed no evidence for either $\text{Cr}=\text{O} \dots \text{Cr}$ or $\text{Cr}-\text{Cl} \dots \text{Cr}$ interactions. The Cr(V) was in a 2D ground state term. Contributions due to Van Vleck paramagnetism (τ_{IP}) were also not expected. Although in the present case susceptibilities could not be measured at different temperatures, the values obtained for the magnetic moments which were close to the spin only value point clearly to the pentavalency of chromium, corroborating the chemical evidences like the oxidation state determined and the other chemical tests. The ESR spectra (figure 1) of the solid powders also pointed to a d^1 state.

The IR spectra reveal the presence of Cr-O and a C_{4v} point group is indicated. For the oxotetrachlorochromate(V) in I, the peaks (in cm^{-1}) at 1005 *m* and 950 *m* are due to $\nu(\text{Cr}=\text{O})$ stretching vibrations (Kon and Sharpless 1965a,b; Ziebarth and Selbin 1970; Seddon and Thomas 1977). The strong and sharp band at 950 cm^{-1} for II and at 928 cm^{-1} for III appears to be due to $\nu(\text{Cr}=\text{O})$ stretching vibrations. In the absence of

Table 1. Analytical and magnetic data of the oxochlorochromates(V).

Compound	Colour	Elemental analysis Found (Calc. %)			Oxidation state	μ_{eff} (B.M.) at 298°C
		Cr	Cl	N		
I $\text{C}_7\text{H}_6\text{N}_2[\text{CrOCl}_4]\text{H}_2\text{O}$ Benzimidazolium oxotetra- chlorochromate(V) monohydrate	Shiny red	15.00 (14.98)	41.00 (40.92)	8.16 (8.10)	5.02 5.00	1.81
II $\text{C}_{18}\text{H}_{12}\text{N}_2\text{H}_2[\text{CrOCl}_5]2\text{H}_2\text{O}$ Biquinolinium oxopentachloro- chromate(V) dihydrate	Yellow	9.62 (9.64)	33.14 (32.90)	4.99 (5.13)	4.99 5.00	1.83
III $\text{C}_{15}\text{H}_{11}\text{N}_3\text{H}_3[\text{CrOCl}_6]$ Terpyridinium oxohexachloro- chromate(V)	Yellow	10.04 (10.06)	41.00 (41.19)	8.10 (8.12)	5.02 5.00	1.78

Along with the scantiness of literature in electronic spectral studies, doubts exist not only in the assignment of bands but even in the number and positions of peaks. Results of electronic spectral measurements in nujol mull along with the IR peak due to $\text{Cr}=\text{O}$ stretch are presented in table 2. The peak around 18 kK has been noted by Kon and Sharpless (1965a, b), Ziebarth and Selbin (1970), and also by Seddon and Thomas (1977). This is a narrower band which is unsplit and of higher intensity than the band

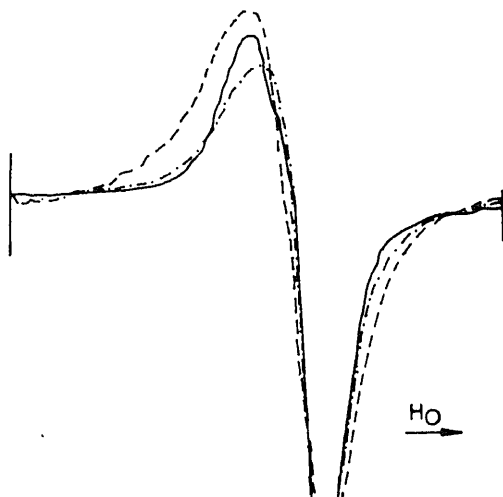


Table 2. IR bands and electronic spectral data of oxochlorochromates(V).

Compound	(Cr=O) cm^{-1}	Electronic spectral peaks in kK (ϵ_M)
I	1005 <i>m</i> , 950 <i>s</i>	23.81, 22.22, 16.39, 15.62, 14.29, 13.0, 12.2 (nujol) 24.39 (1127.8), 22.22 (815.5), 17.25 (98.9), 12.5 (15.2) (acetone)
II	950 <i>s</i>	24.39, 22.72, 18.5, 13.85, 13.0 (nujol) 25.63 (1292.3), 22.72 (357.5), 16.96 (108.7), 11.9 (25.3) (acetone)
III	928 <i>s</i>	25.00, 23.25, 18.08, 14.08, 13.3, 12.3 (nujol)

around 13 kK which appears to be the measure of 10 Dq. The spectra cannot possibly be interpreted in terms of a simple crystal field theory because of the existence of considerable π -bonding between Cr and O. The broad similarities of the mull spectra of the three types of oxochlorochromates(V) appears to indicate the presence of the same point group C_{4v} (viz CrOCl_4).

4. Concluding remarks

From the principle of inorganic symbiosis and from the above considerations, it appears that the nature, particularly the charge, of the counterion dictates the composition of the precipitating solid but discrete ions like $[\text{CrOCl}_5]^{2-}$ or $[\text{CrOCl}_6]^{3-}$ are probably not present. Large univalent cations (Van der Waals radii $> 3.4 \text{ \AA}$) naturally would give crystals like $M [\text{CrOCl}_4]$. But smaller cations $M^1 \leq 1.67 \text{ \AA} (\text{Cs}^+)$ would give $M\frac{1}{2} [\text{CrOCl}_5]$ due to packing requirements. II and III of the present work are probably $(\text{BiquH}_2)\text{Cl} [\text{CrOCl}_4]$ and $(\text{Terpy H}_3)\text{Cl}_2 [\text{CrOCl}_4]$. Without further work particularly x-ray studies, it is hardly possible to say anything definite about the stereo-chemistry of oxochlorochromate(V) anions. The tendency of assigning a definite coordination number and a given stereochemistry from chemical analysis alone may often be misleading as the following example (Zaslow and Ferguson 1967) will show. CuCl_3^- and CuCl_4^{2-} are known in solids and also in solutions but CuCl_3^{3-} is known mainly in the solid state e.g. $(\text{dien H}_3)[\text{CuCl}_5]$ (dien = diethylene triamine) X-ray studies show that the crystals of the latter actually contain $[\text{dien H}_3] \text{Cl} [\text{CuCl}_4]$ and not $[\text{CuCl}_5]^{3-}$.

The packing in a crystal possibly determines part of the stability and some physical features as well. $M\frac{1}{2} [\text{CrOCl}_5]$ ($M^1 = \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+$) type is somewhat hygroscopic, slowly turns pasty and decomposes easily, almost constantly losing chlorine like the $\text{RH} [\text{CrOCl}_4]$ ($R = \text{pyridine, picolines, quinoline etc}$). But some compounds of Cr(V) like the tetraphenyl arsonium, tetraphenyl phosphonium, biquinolinium and terpyridinium compounds are of much better stability and of much less hygroscopicity. It may be that the flexible chains of relatively heavier biquinoline and terpyridine molecules favour more compact packing, thereby increasing the lattice energy and making attack by atmospheric moisture more difficult. Similarly, the much better spherical nature of tetraphenyl arsonium with the similar oxotetrachlorochromate(V) give decent crystals and it is not surprising that the only single crystal study (Gahan *et al* 1977) on a oxochlorochromate(V) compound was that on Ph_4As .

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Effect of various mixed aqueous solvents on the stability constants of Cu(II) chelates with piperidine-2-carboxylic acid

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Abstract. The ligand dissociation constants and the formation constants of Cu(II) piperidine-2-carboxylic acid chelates have been measured in varying proportions of methanol-water, ethanol-water, acetone-water, isopropanol-water and dioxane-water at 30°C and 0.10 M ionic strength. The results are discussed with reference to the change in the dielectric constant of water in the presence of the organic solvent, change in structure and hydrogen bonding in water, relative solvent basicity and proton solvation by the organic solvent. The relatively greater contribution to the stability of the metal chelate by the O-M link as compared to the N-M link has been suggested on the basis of the observed solvent effects on stabilities.

Keywords. Piperidine-2-carboxylic acid; mixed aqueous solvents; solvent effects; formation constants.

1. Introduction

Very little work has been reported on the systematic investigation of dissociation equilibria of ligands and metal chelate formation constants in mixed aqueous solvents. Yet, on the addition of organic solvents, the properties of water undergo marked changes. It has been reported (Irving and Rossotti 1956) that the stabilities of N-M bonds are much less affected than those of the O-M link, on addition of an organic solvent to water. In the present study, we report the effect of solvent characteristics on the formation constants of Cu(II) with piperidine-2-carboxylic acid to determine the relative importance of the effect of solvent properties on compounds containing both O-M and N-M bonds.

2. Experimental

All reagents were AR or GR grade. pH measurements were made using a 'Century' pH meter with a combined glass and calomel electrode. The following solutions (total volume 50 ml) were titrated against standard 0.1 M KOH:

- (i) $\text{HNO}_3 (4.00 \times 10^{-3} \text{ M}) + \text{solvent}$
- (ii) $\text{HNO}_3 (4.00 \times 10^{-3} \text{ M}) + \text{ligand} (2.00 \times 10^{-3} \text{ M}) + \text{solvent}$
- (iii) $\text{HNO}_3 (4.00 \times 10^{-3} \text{ M}) + \text{ligand} (2.00 \times 10^{-3} \text{ M}) + \text{Cu}(\text{NO}_3)_2 (4.00 \times 10^{-4} \text{ M}) + \text{solvent}$

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ionic strength was maintained at 0.10 M by adding calculated amounts of 1 M Na_2CO_3 solution. The metal:ligand ratio was maintained at 1:5. Titrations were carried out in 0, 30, 40, 50, 60 and 70% v/v organic solvent-water mixtures. The organic solvents used were methanol, ethanol, isopropanol, acetone and dioxane. The highest values of the volume proportions were restricted by the solubility of the complex. The titration cell was flushed with pure nitrogen gas previously saturated with the particular solvent used in the titration cell. The pH correction factor (Van Uitert *et al* 1953) at 25°C was obtained for each composition of the five different organic solvents following the procedure of Gentile and Dadgar (1968).

The dissociation constants of piperidine-2-carboxylic acid and Cu(II)-ligand formation constants in the various mixed aqueous solvents were computed using the least squares treatment of the Irving and Rossotti formulae applicable to mixed aqueous solvents, the data is presented in table 1. The average error is ± 0.04 . The values of the thermodynamic constant of the different organic solvent-water mixtures were calculated or obtained from the data given by Akerlof (1932) and Hall and Gibson (1953).

Results and discussion

There is apparently no simple relationship between the stability of complexes and solvent characteristics. As reviewed by Franks and Ives (1966) the structural and related properties of organic solvent-water mixtures are influenced by a complex variety of parameters. Bates *et al* (1966) have indicated that both electrostatic and non-electrostatic effects must be considered to describe adequately the observed trends in dissociation and chelate formation constants. In subsequent work they have characterized the latter effect as the 'solvent basicity' effect. In fact, the non-electrostatic component is probably best characterized in terms of the separate contributions of solvation of the ligand and solvation of the conjugate acid and the base species to the overall changes in dissociation constants. Rorabacher *et al* (1971) have concluded that solvation effects on the conjugate acid and base, while sensitive to short range structural changes, are much less influential in determining the gross solvent effects. The electrostatic component of the solvent effect is assumed to be significant primarily for the protonation of charged bases as a result of the changing solvent dielectric.

In the present study, the expected linear relationship between pK_a and the mole fraction of the organic solvent is observed for each of the five two-component solvent systems. Plots of pK_a vs. mole fraction yield straight lines of different slopes for each solvent system. A plot of pK_a vs. the reciprocal of dielectric constant ($1/D$) likewise, gives rise to linear relationships upto 60% (v/v) organic solvent-water mixtures. This shows that the relationship advanced by Wynne-Jones (1933) is also valid for a single ligand in various mixed solvents throughout a dielectric constant range of 65 to 30. Below a dielectric constant of 30, the pK_a as a function of $1/D$ deviates from linearity. This deviation has been attributed to the fact that the organic solvent-water mixtures are generally treated as homogeneous media of uniform dielectric constant (Glasstone

Table 1. Formation constants of Cu(II) chelates of piperidine-2-carboxylic acid in different mixed aqueous solvents at 30°C and 0.10 M ionic strength.

Solvent composition (%, v/v)	Mole fraction	Reciprocal of dielectric constant $1/D$	pK_a	$\log K_1$	$\log K_2$	$\log \beta_2$
<i>Isopropanol</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.09	0.017	10.56	8.15	6.33	14.48
40	0.13	0.018	10.57	8.41	6.51	14.92
50	0.19	0.021	10.59	8.68	6.68	15.36
60	0.26	0.026	10.65	9.09	7.33	16.42
70	0.28	0.0348	10.71	9.20	7.24	16.44
<i>Dioxane</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.08	0.019	10.53	8.60	6.42	15.02
40	0.12	0.023	10.56	8.72	6.80	15.52
50	0.17	0.029	10.60	8.94	7.83	16.77
60	0.24	0.038	10.75	9.37	7.75	17.12
70	0.25	0.056	10.81	9.92	8.52	18.44
<i>Acetone</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.09	0.016	10.50	7.01	6.40	13.41
40	0.14	0.017	10.55	7.61	6.80	14.41
50	0.19	0.019	10.60	9.19	7.48	16.67
60	0.27	0.225	10.63	9.30	7.80	17.10
70	0.29	0.028	10.67	9.46	8.54	18.00
<i>Ethanol</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.116	0.016	10.53	8.47	7.09	15.56
40	0.169	0.017	10.61	8.58	7.18	15.76
50	0.231	0.019	10.68	8.78	7.25	16.03
60	0.318	0.021	10.73	9.02	7.72	16.74
70	0.355	0.026	10.76	9.37	8.13	17.50
<i>Methanol</i>						
0	0	0.013	10.47	7.49	6.04	13.53
30	0.16	0.015	10.50	8.51	6.94	15.45
40	0.23	0.016	10.52	8.62	6.91	15.53
50	0.30	0.017	10.55	8.74	7.03	15.77
60	0.40	0.019	10.59	8.95	7.23	16.18
70	0.47	0.022	10.63	9.14	7.86	17.00

dielectric constant for the different organic solvent-water mixtures. A linear relationship is noted upto 60% (v/v) of the organic solvent-water mixtures after which deviations are observed. However, due to solubility restrictions, the $\log K$ vs. $1/D$ relationship could not be investigated beyond 70% v/v. An interesting feature of the linear relationship is that for the alcohol water mixtures (methanol, ethanol and isopropanol-water), the slopes of the straight lines are identical, but are markedly

and dioxane are in another group with respect to their solvent effect on metal chelation (Gentile *et al* 1963).

A plausible explanation for the above behaviour on the basis of the bulk and local dielectric constants of the media has been advanced by Gentile and Dadgar (1968). It appears that for the alcohol-water mixtures, the local dielectric constant is lower than that of acetone-, dioxane-water mixtures. The lower the local dielectric constant, the higher is the expected $\log K$ value and this was found to be true experimentally. However, it would be naive to justify this observed trend in $\log K$ values on the basis of the above explanation alone, and hence, a better understanding of the influence of the other factors is essential.

It has been suggested (Irving and Rossotti 1956) that since O-metal bonds are more influenced by the composition of the solvents than N-metal bonds, the effect of solvent composition on the stabilities of chelates containing the O-metal-N link might give an indication of the relative importance of these bonds. The $\log \beta_2$ of Cu(II) with piperidine-2-carboxylic acid in aqueous medium at 30°C and 0.1 M ionic strength is 13.53. The highest value for $\log \beta_2$ observed for the same system in 70 % v/v dioxane-water is 18.44. The overall stability constant $\log \beta_2$ in the aqueous and the dioxane-water mixtures varies by 4.91 log units. This may suggest that the O-M bond in the chelate is stronger than the N-M bond.

4. Conclusions

The different solvent characteristics mentioned above influence the pK_a of the ligand in the following manner:

- (i) pK_a increases with decrease of the dielectric constant and vice versa;
- (ii) on decreasing the extent of hydrogen bonding in water by adding an organic solvent, the proton accepting property of water increases. Hence the dissociation constant (K_a) increases or the ligand becomes a weaker base;
- (iii) increased proton solvation by the organic solvent increases the pK_a of the ligand.

For a particular composition of solvent-water mixture say 60 %, v/v, the reciprocal of the dielectric constant changes in the following order:

dioxane-water > isopropanol-water > acetone-water > ethanol-water > methanol-water.

For the same v/v percentage of the organic solvent-water mixture, the order of pK_a is in the order:

dioxane-water > isopropanol-water > ethanol-water > acetone-water > methanol-water.

This is the same as the order of the reciprocal of dielectric constants except that acetone and ethanol have exchanged places.

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Stability of the ternary complexes of inosine in solution

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Abstract. The interaction of Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Mg(II) and Ca(II) with inosine and secondary ligands histidine and glycine in a 1:1:1 ratio was determined by potentiometric equilibrium measurements at 35°C and 0.10 M (KNO₃) ionic strength. The stability constants of the ternary complexes of xanthosine with histidine and glycine are also included for effective comparison. The ternary complexes were found to be stabler than the corresponding binary complexes. This higher stability of the ternary complexes is measured in terms of $\Delta \log K$ which is the difference between the overall 1:1:1 stability constant and the corresponding 1:1 constant. Histidine forms stabler ternary complexes with inosine than does glycine. This is attributed to the π -accepting capacity of the imidazole ring of histidine and also to the stacking interaction between the purine part of inosine and the imidazole moiety of histidine.

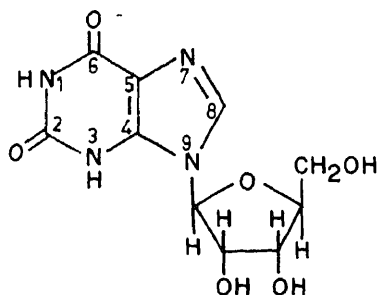
Keywords. Inosine; histidine; glycine; ternary complexes; stacking interactions.

1. Introduction

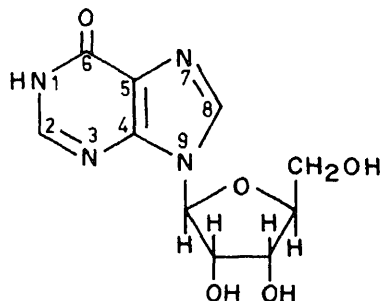
During recent years considerable attention has been focussed on the ternary complexes of nucleosides and nucleotides in solution, due to their importance in many biological processes (Taqui Khan and Rabindra Reddy 1972, 1973; Rabindra Reddy *et al* 1976, 1978, 1979; Fischer and Sigel 1980; Scheller *et al* 1981; Arena *et al* 1983; Sigel *et al* 1983). Under biological conditions many potential ligands are likely to compete for metal ions and, as such, multiligand equilibria exist in solution and hence mixed ligand or higher order complexes are formed. Consequently, the determination of the stability of the ternary complexes will help in understanding the specific and selective interactions that occur in many biochemical reactions. Although many published data are available on the metal complexes of purine and pyrimidine bases and nucleotides (Izatt *et al* 1971; Taqui Khan and Rabindra Reddy 1972, 1973; Taqui Khan and Krishnamoorthy 1974; Taqui Khan and Rabindra Reddy 1975, 1976; Sigel 1975; Fischer and Sigel 1980; Arena *et al* 1983; Sigel *et al* 1983; Lippert 1983; Rabindra Reddy *et al* 1983a,b), very little is known about nucleoside complexes in solution. Nucleosides provide a link between bases and nucleotides, and hence any information on complexation properties of nucleosides will be worthwhile. In view of this, we systematically investigated the interaction of metal ions with nucleosides in solution, in the hope of evolving a better understanding of the base versus phosphate binding.

Earlier work on nucleosides is mainly restricted to xanthosine (Rabindra Reddy *et al* 1976, 1978, 1979, 1984; Rabindra Reddy and Harilatha Reddy 1983, 1985; Rabindra

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XANTHOSINE



INOSINE

Reddy and Venugopal Reddy 1983) and this study has provided useful information on the nature of metal nucleic acid interactions. However, the work on inosine was confined only to dissociation constants and the determination of the binary stability constants (Rabindra Reddy *et al* 1983b; Albert 1953; Tu and Friederich 1968). Here we report the data obtained from a detailed physico-chemical investigation of Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Mg(II) and Ca(II) with inosine and biologically important secondary ligands, histidine and glycine, in a 1 : 1 : 1 ratio at 35°C and 0.10 M (KNO₃) ionic strength.

Inosine resembles xanthosine very closely (structures given above). Earlier investigations have shown that xanthosine binds to the metal through O(6) and N(7) (Rabindra Reddy *et al* 1978). No doubt, inosine is also expected to bind through the same sites, but the extent of interaction may vary due to the presence of an additional donor group O(2) in xanthosine. Therefore, any comparison of the stability data for the two systems will be highly informative. Such interactions and comparisons will hopefully pave the way for understanding the metal coordination in nucleosides and thus may help in the correct assignment of the binding sites of nucleic acid components.

2. Experimental

Inosine, histidine and glycine were obtained from the Sigma Chemical Company (USA). Transition and alkaline earth metal ions were of Analar grade and were standardised volumetrically by titration with the disodium salt of EDTA in the presence of a suitable indicator as outlined by Schwarzenbach (1957).

The experimental method employed consisted of a potentiometric titration of metal and inosine with a secondary ligand histidine or glycine, in a 1 : 1 : 1 ratio at 35° ± 0.1°C and 0.10 M ionic strength, with standard NaOH solution. The experimental conditions maintained were similar to those described earlier (Rabindra Reddy *et al* 1984).

To calculate the stability constants of the ternary complexes of Cu(II), Ni(II), Co(II), (II) and Mn(II) with inosine and histidine in a 1:1:1 ratio the following equations are used (excluding the charges):



together with the related equilibria:



$$K_{MHLA}^M = \frac{T_M - [M]}{[M][L][HA]} \quad (3)$$

where:

$$[M] = a'A \text{ or } b'L$$

$$L = \frac{a'\alpha}{a'b + b'a}; \quad HA = \frac{[H^+]}{K_{2aA}} \cdot A; \quad A = \frac{b'\alpha}{a'b + b'a}$$

$$\alpha = (2-m)T_L - H^+ + OH^-; \quad a = \frac{2[H^+]^2}{K_{aA} \cdot K_{2aA}} + \frac{[H^+]}{K_{2aA}};$$

$$a' = \frac{[H^+]^2}{K_{aA} \cdot K_{2aA}} + \frac{[H^+]}{K_{2aA}} + 1; \quad b = \frac{2[H^+]}{K_{aL}}; \quad b' = \frac{[H^+]}{K_{aL}} + 1$$

T_M = total concentration of the metal ion species in solution;

T_L = total concentration of the ligand species in solution;

$[M]$ = concentration of the unbound metal ion;

m = moles of base added per mole of metal ion;

α = monoanion of inosine;

A = neutral histidine;

where the subscripts A and L represent histidine/glycine and inosine, respectively. This

equation was also used for the ternary complexes of Cu(II) with inosine and glycine.

However, for the ternary complexes of Mg(II) and Ca(II) with inosine and histidine

in a 1:1:1 ratio the following equations were used (deleting charges);



together with related equilibria



$$K_{MLA}^{MA} = \frac{T_M - [M]}{[M][L][A]} \quad (6)$$

$$L = \frac{a'\alpha}{a'b + b'a}; \quad A = \frac{b'\alpha}{a'b + b'a}; \quad [M] = a'A \text{ or } b'L$$

$$\alpha = (2-m)T_L - H^+ + OH^-; \quad a = \frac{2[H^+]}{K_{2aA}} + 1; \quad a' = \frac{[H^+]}{K_{2aA}} + 1$$

$$b = \frac{2[H^+]}{K_{aL}} + 1; \quad b' = \frac{[H^+]}{K_{aL}} + 1$$

Ni(II), Co(II), Zn(II), Mn(II), Mg(II) and Ca(II) with inosine and glycine in a 1:1:1 ratio.

4. Results and discussion

4.1 Metal-inosine-histidine system

The mixed ligand titration curve of Cu(II)-inosine-histidine in a 1:1:1 ratio given in figure 1C shows an inflection at $m = 2$ indicating the simultaneous formation of a 1:1:1 mixed ligand complex in the buffer region between $m = 0$ and 2 (m = moles of base added per mole of the metal ion). The constant K_{MHLA}^M was calculated using (3) and presented in table 1. Similar trends were observed for all the metal ion studied except for Mg(II) and Ca(II) in which [figure 1B for Mg(II)] an inflection was obtained at $m = 1$. Accordingly, it was assumed that a ternary complex was formed from the monoprotonated binary (1:1) histidine complex ($m = 0$ and 1) and the constant K_{MLA}^{MHA} was calculated in the buffer region between $m = 1$ and 3, using (6). The constants so calculated are listed in table 1.

4.2 Metal-inosine-glycine system

The titration curve of Cu(II) with inosine and glycine in a 1:1:1 ratio (figure 2P) resulted in an inflection at $m = 2$ indicating the simultaneous formation of the mixed

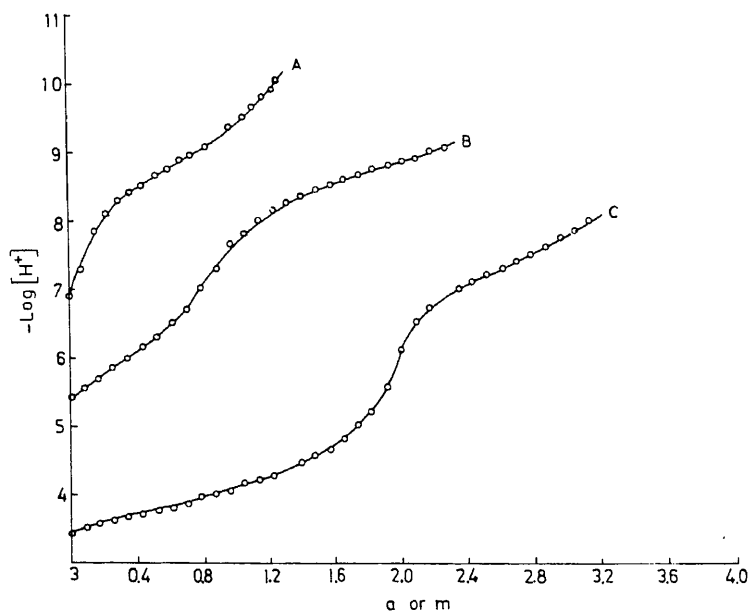


Figure 1. Mixed ligand titration curves for Cu(II)-inosine-histidine and Mg(II)-inosine-histidine in a 1:1:1 ratio at 35°C and $\mu = 0.10$ M (KNO_3) [A = Inosine free ligand; B = Mg(II)-inosine-histidine; C = Cu(II)-inosine-histidine; a = moles of base added per mole

Table 1. Stability constants of the ternary complexes of inosine and xanthosine with histidine and glycine.

M(II)	M:inosine:glycine (1:1:1)		*M:xanthosine:glycine (1:1:1)		M:inosine:histidine (1:1:1)		**M:xanthosine:histidine (1:1:1)		$\Delta \log K$	M:Ino:Gly (1:1:1)	M:Xan:Gly (1:1:1)	* $\Delta \log K$
	K_{MHLA}^M	K_{MLA}^{MH4}	K_{MHLA}^M	K_{MLA}^{MH4}	K_{MHLA}^M	K_{MLA}^{MH4}	K_{MHLA}^M	K_{MLA}^{MH4}				
Cu	12.57	—	12.8	—	14.55	—	13.19	—	—	—	1.13	—
Ni	—	11.23	10.9	—	13.18	—	11.84	—	2.13	2.13	2.06	—
Co	—	10.56	—	3.0	11.60	—	10.11	—	2.22	2.22	0.49	—
Zn	—	10.89	—	2.8	11.47	—	9.05	—	2.60	2.60	0.59	—
Mn	—	10.72	—	2.8	11.68	—	—	2.9	—	—	0.23	—
Mg	—	8.52	—	2.5	—	9.13	—	2.79	—	—	0.27	—
Ca	—	8.23	—	2.6	—	8.88	—	2.76	—	—	0.39	—

$\mu = 0.10 \text{ M (KNO}_3\text{)}$; temperature = 35°C; K values are log K; deviations are omitted for clarity.

* Rabindra Reddy and Harilatha Reddy 1983

** Rabindra Reddy and Harilatha Reddy 1985

complex in the buffer region between $m = 0$ and 2 and the monoprotonated constant was calculated using (3); values thus determined are presented in table 1.

In figure 2 Q is the mixed ligand titration curve of Mg(II)-inosine-glycine in a 1:1:1 ratio. This curve indicated an inflection at $m = 1$. Accordingly, it was assumed that a ternary complex was formed from the monoprotonated (1:1) glycine ($m = 0$ and 1) complex, and the constant was calculated in the buffer region between $m = 1$ and 3 with the help of (6). The constants thus calculated are recorded in table 1. Similar results were also obtained for all the other metal ions studied.

The stability constants presented in table 1 show that the ternary complexes are more stable than their corresponding binary complexes, a trend which is not expected based only on the statistical considerations. This is because of the destabilization caused by the ligand repulsion being lower in the ternary complexes than in the binary complexes. This extra stability of the ternary complexes is usually measured in terms of $\Delta \log K$. $\Delta \log K$ is defined as the difference in the overall 1:1:1 stability constants and the corresponding constants of the 1:1 complexes. So the positive values of $\Delta \log K$ show that the ternary complexes are more stable than the binary complexes. The negative values of $\Delta \log K$ generally result from the absence of electronic effects or specific interactions between the two ligands in the ternary system. However, it should be noted that the negative values of $\Delta \log K$ do not preclude the formation of the ternary complexes in solution.

The $\Delta \log K$ values for Ni(II)-inosine-glycine, Zn(II)-inosine-glycine and Co(II)-inosine-glycine systems are reported in table 1. It can be seen from the table that the $\Delta \log K$ values for Zn(II) are more positive indicating the higher stability of Zn(II), as compared to the Ni(II) and Co(II) systems. This higher stability of Zn(II) exemplifies its

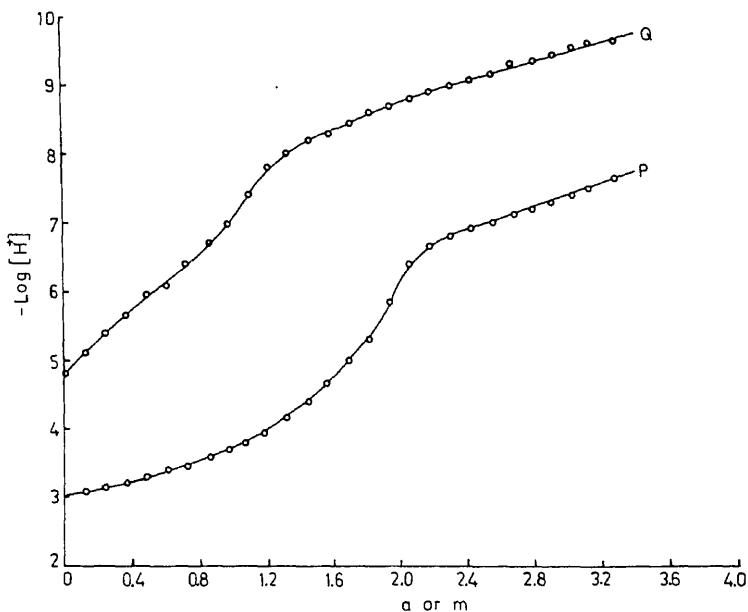


Figure 2. Mixed ligand titration curves of Cu(II)-inosine-glycine and Mg(II)-inosine-

importance in many biochemical reactions. The $\Delta \log K$ values for the other systems under the present investigation could not be computed owing to the formation of different types of complexes in the ternary and binary systems. Meaningful information can, however, be obtained by comparing the absolute values of the stability constants of the ternary and binary systems. For e.g., the data in table 1 indicate the higher stability of the ternary complexes as compared to their binary counterparts. This enhanced stability of ternary complexes is due to various factors like charge neutralization, electronic or cooperative effects (formation of π bonds), and the stacking interaction (a phenomenon expected to occur between the aromatic moieties of the two ligands).

Also, it was shown in our earlier investigation that in mixed ligand complexes the reaction between the metal ion and the secondary ligands containing heteroaromatic nitrogen and oxygen donor atoms result in the formation of stabler ternary complexes than with the ligands containing pure nitrogen and oxygen donor atoms (Rabindra Reddy and Harilatha Reddy 1983). Although the secondary ligands in the ternary complexes (1:1:1) of both metal-inosine-histidine and metal-inosine-glycine have mixed N/O donor groups, the stabilities of histidine complexes are found to be higher than of the glycine complexes. This is due to (a) the stacking interaction, (b) the π accepting capacity of the imidazole ring of histidine, and (c) involvement of all the available donor sites in metal coordination. Stacking interaction occurs between the purine part of inosine and the imidazole moiety of histidine. This type of interaction was also observed earlier (Scheller *et al* 1981; Rabindra Reddy and Venugopal Reddy 1983; Rabindra Reddy *et al* 1984). The π accepting capacity of the imidazole ring in histidine will influence the transfer of electrons from the metal ion to the imidazole ring and this results in an increase in the positive charge on the metal ion than in the binary complex, and thereby increases the metal interaction in the ternary system. Thus, in the metal-inosine-histidine system a cooperative effect exists between the two aromatic rings resulting in the formation of stabler ternary complexes. Glycine, being an aliphatic ligand, can not participate in stacking interaction and also does not exert any cooperative effect on the aromatic ring of the inosine. This accounts for its lower stability. Also, the difference in the stability constants for the 1:1 Cu-glycine and 1:1 Cu-histidine systems is about 1.4 log K units. The same order of magnitude is observed in the $\Delta \log K$ values of ternary complexes of glycine and histidine with inosine. This clearly shows that histidine does not act like glycine but as a terdentate ligand involving all its available donor atoms in metal binding, otherwise the difference between them would not have been of this order of magnitude (Rabindra Reddy and Harilatha Reddy 1985).

It is of interest here to compare the $\Delta \log K$ values of the metal-inosine-glycine system with those of the metal-xanthosine-glycine system. The $\Delta \log K$ values for the inosine system are more positive than the corresponding complexes of xanthosine (Rabindra Reddy and Harilatha Reddy 1983). This shows that the ternary complexes of inosine are more favoured than the ternary complexes of xanthosine. The same conclusions can also be drawn from the absolute values of their stability constants. This may be due to the presence of an additional donor group O(2) in xanthosine which may compete for metal-coordination along with the O(6) and N(7) positions. Although, the O(2) participation in ternary complexes is not favoured sterically, it may exert an influence on the O(6) and N(7) binding positions thus making the metal interaction less effective and resulting in lower stability of the ternary complexes of xanthosine in

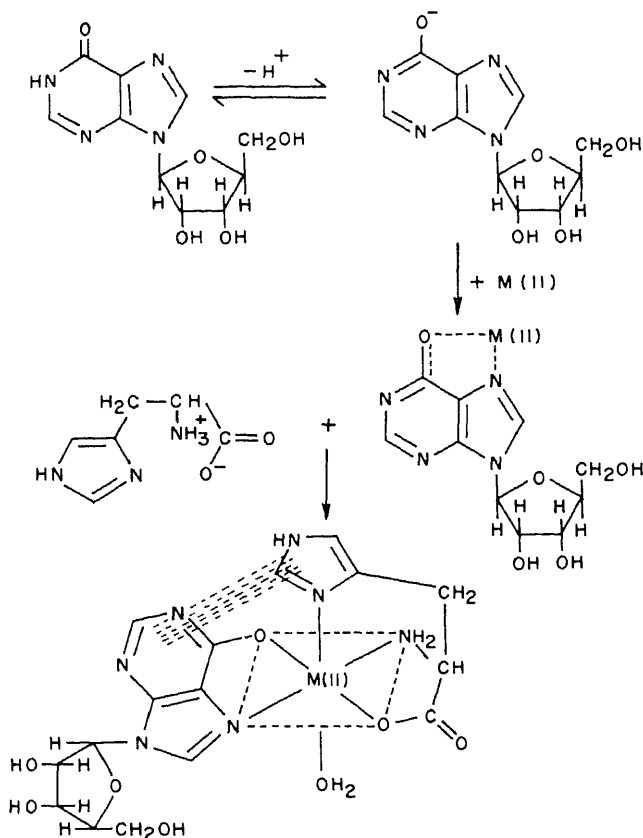


Figure 3. Tentative structure showing the proton dissociation and metal association reactions of inosine (binary and ternary) (R = Ribose).

It is important here to briefly mention the stabilities of xanthosine and inosine in their binary systems. Xanthosine (Rabindra Reddy *et al* 1976) forms stabler complexes as compared to inosine (Rabindra Reddy *et al* 1983b) with all the metal ions studied. This is in accord with the basicities of the ligands concerned. The higher stability of binary xanthosine complexes may also be partly responsible for the lower stability in ternary complexes.

A tentative structure showing the proton dissociation and metal association reactions of inosine (binary and ternary) given in figure 3 depicts the differences in the solvation energies of the above systems. Here, the entropy values rather than the enthalpy values may be responsible for the control of stabilities in solution.

Acknowledgement

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Kinetic-spectrophotometric determination of manganese

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Abstract. A simple and fairly selective kinetic method has been developed for the determination of manganese(II) based on its catalytic activity on the autoxidation of *o*-hydroxyphenylthiourea (OHPTU). It is found that the rate of the reaction is proportional to the concentration of manganese(II) ions. The reaction is carried out in a borate buffer of pH 7.5 and determined effectively in the range of 0.05–0.50 µg of manganese per ml. The methods of tangents and of fixed time are employed. The former method is more accurate than the latter. The present method has been applied to foodstuff like cabbage, tomato and potato wherein manganese plays a vital role in various physiological functions. Many associated metal ions do not interfere in the determination.

Keywords. Manganese(II); *o*-hydroxyphenylthiourea; catalytic action; autoxidation.

Introduction

The concept of kinetic methods of analysis, especially those based on catalysed reactions, for determination of trace elements has gained considerable importance in analytical chemistry as is evident from the literature (Mottola and Mark 1982; Matsimirskii 1966; Harris and Kratochvil 1981; Laitinen and Harris 1975) because of their simplicity, sensitivity and fairly wide selectivity over the activation analysis and atomic absorption spectrophotometric methods. In the present investigation, the catalysed autoxidation reaction is monitored with an ordinary spectrophotometer which is simple, less expensive and easily available to researchers in developing countries like India. The present method can be well adopted to determine manganese, an essential micronutrient, in foodstuff.

Experimental

1. Reagents

All the chemicals used are of AnalaR grade.

Manganese(II) solution: About 3.0768 g of manganese sulphate monohydrate is weighed exactly, dissolved and made up to 250 ml with distilled water. The solution is standardised with EDTA (Vogel 1962).

o-Hydroxyphenylthiourea (OHPTU): It is prepared as per the standard procedure given in Beilstein (1943). The reagent solution (1 mg/ml) is prepared in 95% ethanol just before use.

Michaeli's borate buffer of pH 7.5 is prepared.

2.2 Apparatus

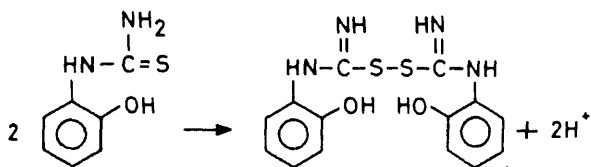
Toshniwal Spectrophotometer model RL02 and Elico pH meter model L1-10 were used in the present investigation. The plant samples were dried in a muffle furnace (Tempo).

2.3 Procedure

An aliquot of manganese solution (1.0–12.5 μg) was transferred to a 25 ml standard flask. 2.5 ml of the reagent solution (1 mg/ml) and 10 ml of borate buffer (pH 7.5) were added to the same flask. The solution was made up to the mark with distilled water and absorbance of the solution was measured with time using a reagent blank at 416 nm.

3. Results and discussions

OHPTU undergoes autoxidation with the formation of yellow coloured disulfide, 1,1'-dithiobis *N*-(*o*-hydroxyphenyl)-formamidine, which is confirmed by analysis (Santhanam 1964; Feigl 1966). The reaction may be represented as



The above reaction is very slow and the rate of the reaction increases abruptly in the presence of microquantities of manganese. The increase in the concentration of manganese increases the rate of the catalysed oxidation and it is found from the results that the rate of the reaction is proportional to the concentration of manganese. The λ_{max} values for OHPTU and its disulphide are 280 and 416 nm respectively. Despite the wide difference in λ_{max} values, the reagent has some absorbance at 416 nm. However, this can be compensated by measuring absorbance against a reagent blank. In the present studies the 'method of tangents' is followed. The plot of slope against concentration of manganese is linear (figure 1) in the range of 0.05–0.50 $\mu\text{g}/\text{ml}$.

The reaction rate is sufficiently fast in borate buffer of pH 7.5–8.0. The catalysed autoxidation is slow below pH 5.0 and the uncatalysed reaction itself is fast above pH 10.5. The rate of the reaction is enhanced on raising the temperature of the system. Hence, the reaction system is maintained at laboratory temperature by keeping it in a thermostat bath. The sensitivity of the reaction is improved by the addition of 1 ml of

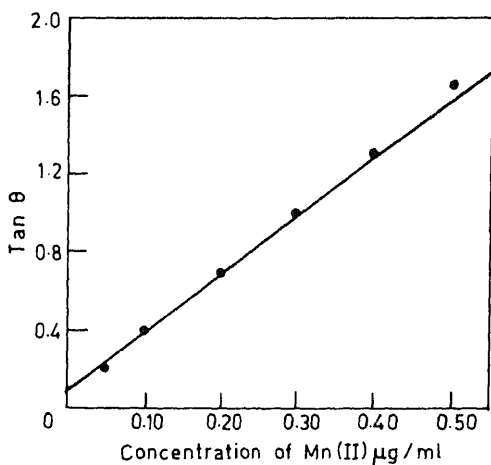


Figure 1. Calibration curve for determination of manganese(II) by the tangents method.

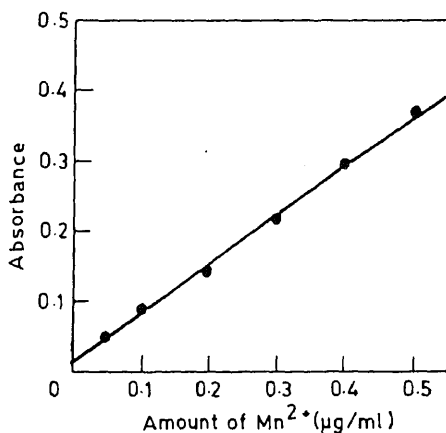


Figure 2. Calibration curve for determination of manganese(II) by the fixed time method.

for 0.3 μg of manganese per ml. It is observed that 2.0 mg of the reagent is sufficient for the investigation.*

Metal ions like aluminium(III), molybdenum(VI), tungsten(VI), gold(III), platinum(VI), vanadium(V) and zinc(II) do not interfere upto 35-fold excess by weight whereas cobalt(II), palladium(II) and silver(I) interfere by slightly enhancing the reaction rate when they are present below 20-fold excess. The interference of iron is eliminated by the addition of fluoride. Among the anions chloride, sulphate, nitrate and fluoride have no effect on the determination.

Table 1. Determination of manganese in some kinds of food stuff

Sample	Mn(II) found by	
	the present method ($\mu\text{g/g}$)*	the periodate method ($\mu\text{g/g}$)
1. Cabbage (<i>Brassica oleracea capitata</i>)	11.9	12.1
2. Potato (<i>Solanum tuberosum</i>)	5.8	5.8
3. Tomato (<i>Lycopersicon esculentum</i>)	9.8	9.7

*An average value for five determinations.

4. Application

The present method has been applied for the determination of micro quantities of manganese present in plant materials like cabbages, tomatoes and potatoes. The samples are thoroughly washed, dry ashed and made into solution as per the procedure of Chapman and Pratt (1961). The amounts of manganese in the above samples are computed from the calibration plot and are comparable with the values obtained by the standard periodate method (Vogel 1962) for the same samples (table 1).

5. Conclusions

The method developed here is simple and does not require any sophisticated or complicated equipment. The accuracy of the method is improved by following the 'method of tangents'. This method is applied to plant materials for determination of the manganese present.

Acknowledgements

One of the authors (S J Rao) is thankful to the UGC, New Delhi for the award of a fellowship.

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Kinetics and mechanism of the interactions of imidazole and benzimidazole with *cis*-diaquo(nitrilotriacetato)cobalt(III)

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Abstract. The kinetics of the anation of *cis*-diaquo(nitrilotriacetato)cobalt(III) with imidazole (IMZ) and benzimidazole (BIMZ) have been studied in the pH range 6.10–7.10 and 5.60–6.85 respectively at $\mu = 0.1$ M and in the temperature range 40–60°C. Both reactions produce the bisubstituted product but the entry of the first ligand is rate determining in each case. The pH dependence of rate shows that the neutral ligand reacts with both the acid and the base forms of the complex, the reactivity of the base form being slightly higher in each case. The pseudo first-order rate constants show a non-linear dependency on the concentration of incoming ligand at a particular pH. A pure *D* (dissociative) mechanism rather than *I_d* (dissociative interchange) is operative which is supported by previously reported results of imidazole substitution reactions.

Keywords. Anation; *cis*-diaquo(nitrilotriacetato)cobalt(III); imidazole; benzimidazole; pure dissociative conjugate base mechanism.

Introduction

Much of the studies on substitution reactions at octahedral metal centres are confined to the substituted or unsubstituted cobalt(III) amine complexes (Wilkins 1974; Moore 1977). Complexes with ligands having fewer than four donor nitrogens are not well explored. In keeping with this, we have attempted to follow the reaction of *cis*-diaquo(nitrilotriacetato)cobalt(III) with imidazole and benzimidazole. Prior to this work Thacker and Higginson (1974) have made some investigations on the reaction of this complex with a few non-metallic substrates in aqueous solution, and Meloon and Harris (1977) have studied its formation from the acid catalysed hydrolysis of the dinuclear di- μ -hydroxo-bis(nitrilotriacetato)cobalt(III) species. The choice of imidazole and benzimidazole as possible substituents is due to the fact that the imidazole as a histidine moiety functions as ligand toward transition metal ions in a variety of biologically important molecules (Martin 1974) while substituted benzimidazole is an integral part of the structure of vitamin B₁₂ (Preston 1974). Consequently, a massive effort is being expended currently on the reactivity of imidazole and benzimidazole with various transition metal ions and complexes (Randall and Alberty 1967; Shepherd and Laube 1973; Krishnamurthy 1978; Thompson and Krishnamurthy 1979).

2. Materials

Imidazole and benzimidazole have been purchased from BDH and all other chemicals are of reagent grade. The mononuclear *cis*-[Co(NTA)(OH₂)₂] (H₃NTA = nitrilotriacetic acid) is generated *in situ* by adding dilute nitric acid to K₂[Co₂(NTA)₂(OH)₂] following Meloon and Harris (1977). The molar extinction coefficients of the diaquo species are 208 M⁻¹ cm⁻¹ and 221 M⁻¹ cm⁻¹ at 398 and 554 nm respectively. These are exactly half of that shown in figure 2(I) of Meloon and Harris's (1977) report since the dissociation of one mole of the binuclear species results in two moles of the mononuclear complex. Fresh solutions of the diaquo species have been prepared each day as it decomposes by reduction on long storage.

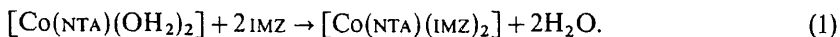
3. Methods

A Pye-Unicam SP8-150 spectrophotometer has been used for all absorption spectral studies. The kinetics are followed by measuring the change in absorbance of the reaction mixture at definite time intervals. For this a little of the mixed solution has to be quickly withdrawn from the reaction vessel (kept in a thermostatic bath) with the help of a jacketed pipette containing pieces of ice to quench the reaction. Initial pH adjustments are done by additions of a little 0.01 M NaOH or HNO₃, employing the self-buffering capacity of the excess imidazole or benzimidazole in the experimental pH range. The pH measurements have been carried out with a digital Beckman (Model 4500) pH-meter. Ionic strength is adjusted to 0.10 M by using recrystallized NaClO₄.

4. Results and discussion

4.1 Reaction of *cis*-[Co(NTA)(OH₂)₂] with imidazole

During the course of the reaction of the complex with excess imidazole (2×10^{-4} – 2×10^{-3} M), the absorption maximum characteristics of the diaquo species at 554 nm decreases in intensity and that at 526 nm increases in intensity resulting in the appearance of two maxima at 526 nm (log ϵ , 2.25) and 368 nm (log ϵ , 2.29). These changes are accompanied by a clear set of isosbestic points at 536, 444 and 372 nm (figure 1). Results of the spectrophotometric titration of imidazole show definite break at 1:2 stoichiometry for the diaquo(nitrilotriacetato)cobalt(III): imidazole (figure 2). Thus the overall reaction is represented as



Under the conditions of kinetic study to be delineated later, the reaction goes to completion as revealed from the constancy of A_∞ values at a particular cobalt(III) complex concentration but with varying amounts of the heterocyclic base.

In this reaction system there was the possibility of observing two consecutive

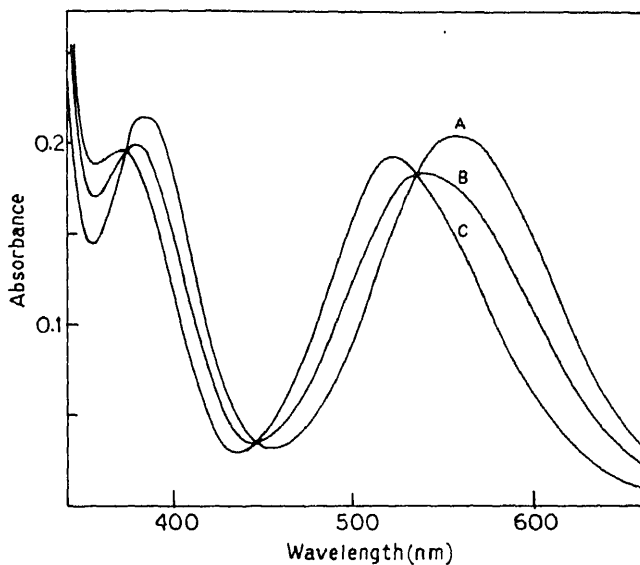


Figure 1. Absorbance spectral change for the system *cis*-[Co(NTA)(OH₂)₂]/imidazole at 50°C pH = 6.50, $\mu = 0.1$ M, [Complex]_T = 1×10^{-3} M, [IMZ]_T = 0.1 M, A—spectrum of *cis*-[Co(NTA)(OH₂)₂], C—spectrum recorded after keeping the mixture for 24 hr.

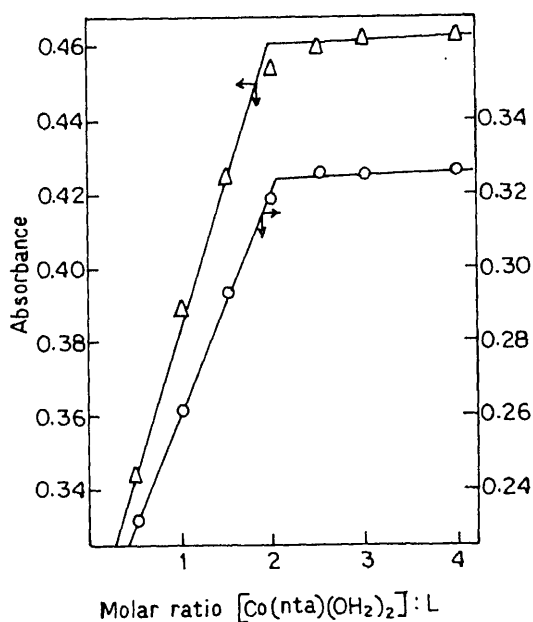


Figure 2. Spectrophotometric determination of the stoichiometry of the complexes of

reaction $A \rightarrow B \rightarrow C$, the presence of isobestic points as described earlier (figure 1) throughout the reaction is indicative that the first stage $A \rightarrow B$ is rate determining with no measurable build-up of species B and (iii) the plots of k_{obs} vs $[\text{IMZ}]_T$ which are highly curved in nature show zero intercepts (vide supra). It is tempting to speculate that the first imidazole increases the affinity of the metal ion for the second imidazole molecule, i.e., a *cis*-labilising effect caused by the apparent electron density around nitrogen of the imidazole ring is operative.

The kinetics of the reaction have been studied at 580 nm with various concentrations of cobalt(III) (4×10^{-5} – 1×10^{-4} M), imidazole (2×10^{-4} – 4×10^{-3} M) and hydrogen ions (7.94×10^{-8} – 7.94×10^{-7} M) and the results are shown in table 1. It should be mentioned here that for the runs in which imidazole is not in greater than five-fold excess with respect to complex concentration, the values of k_{obs} are deduced from the initial portions of the rate data where reasonable first-order kinetics prevail. Except in those runs the plots of $\log(A_t - A_\infty)$ vs time t are linear for more than three half-lives of the reaction. The first acid dissociation constant of $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ has been found by Thacker and Higginson (1974) to be 1.95×10^{-7} M ($pK_1 = 6.71 \pm 0.01$) at 25°C and we have found this pK_1 to be nearly temperature independent. The reported pK_a values (Sillen and Martell 1971) of imidazole are 6.70, 6.49 and 6.35 at 40, 50 and 60°C respectively. So the acid dependency of the rate is analysed as the occurrence of (2)–(7).

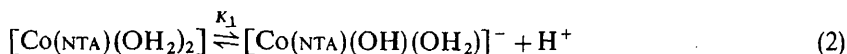
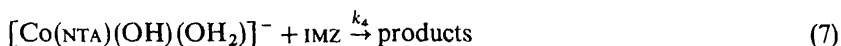
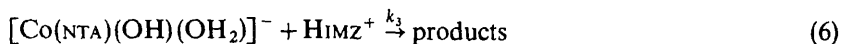
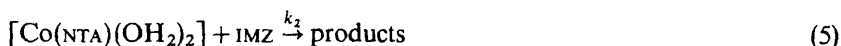


Table 1. Kinetic data for the reaction of *cis*- $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ with imidazole.

Temperature ($^\circ\text{C}$)	$[\text{IMZ}]_T$ ($\times 10^4$ M)	k_{obs} ($\times 10^5 \text{ sec}^{-1}$)	k_a ($\times 10^5 \text{ sec}^{-1}$)	k_b/k_c ($\times 10^5$)
40	2	1.69	2.70	2.24
	3	1.96		
	4	2.23		
	5	2.30		
	8	2.30		
	12	2.38		
	20	2.53		
50	2	4.16	8.25	5.29
	3	5.44		
	4	5.76		
	5	6.08		
	8	6.65		
	10	6.65		
60	2	11.00	17.85	4.64
	3	12.22		
	4	13.70		
	5	14.21		
	8	15.28		
	12	16.09		
	20	16.88		

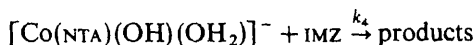
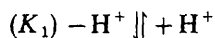
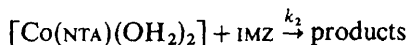
pH = 6.10 ± 0.04 , ionic strength $\mu = 0.1$ M (NaClO_4), $[\text{complex}]_T = (4-10)$



At relatively low pH (< 5) repetitive spectral scanning indicates no usual substitution (at $\approx 60^\circ\text{C}$), rather slow reduction to Co^{2+} is noticed by the gradual diminution of absorption intensities. This observation precludes any reaction path arising from the k_1 term and (8) can be derived.

$$k_{\text{obs}} = \frac{(k_2 + k_3 K_1 K_a^{-1})[\text{H}^+]^{-1} + k_4 K_1 [\text{H}^+]^{-2}}{(1 + K_1 [\text{H}^+]^{-1})(1 + [\text{H}^+] K_a^{-1})[\text{H}^+]^{-1}} \quad (8)$$

Plots of $k_{\text{obs}}(1 + K_1 [\text{H}^+]^{-1})(1 + [\text{H}^+] K_a^{-1})$ vs $[\text{H}^+]^{-1}$ at imidazole concentrations $(10 \times 10^{-4} \text{ M})$ yield curves rather than straight lines which indicate the invalidity of the composite scheme (Tsukahara *et al* 1982). Earlier workers (Krishnamurthy 1978; Randall and Alberty 1967) have shown that the species HIMZ^+ is not at all reactive in the substitution reactions of imidazole with tetra-*p*-sulphophenylporphinato-rhodium(III) and also with aquocobalamin. Participation of neutral imidazole with the acidic and basic forms of the complex, as shown below, seems the possible pathway.



As will be discussed later, the reaction attains a limiting rate at $[\text{IMZ}]_T > 5 \times 10^{-4} \text{ M}$, i.e., the reaction becomes independent of imidazole concentrations at such conditions and therefore behaves as an aprotic substituent. The observed rate is given by

$$k_{\text{obs}} = \frac{k_2 [\text{H}^+] + k_4 K_1}{K_1 + [\text{H}^+]}. \quad (9)$$

At $[\text{IMZ}]_T = 1 \times 10^{-3} \text{ M}$, $\mu = 0.1 \text{ M}$ and temperature 50°C , plot of $k_{\text{obs}}(K_1 + [\text{H}^+])$ vs $[\text{H}^+]$ gives very good linear fits (figure 3). The ratio k_4/k_2 is 3.00 ± 0.09 which indicates that the hydroxoquo species is only slightly more reactive than its diaquo analogue. The pseudo first-order rate constants show non-linear dependency on the total concentrations of imidazole at a particular $[\text{H}^+]$. The observed rate law is

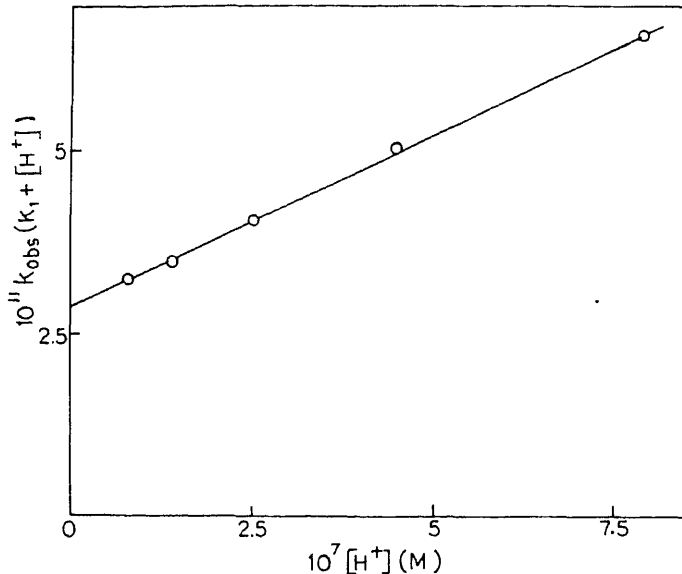
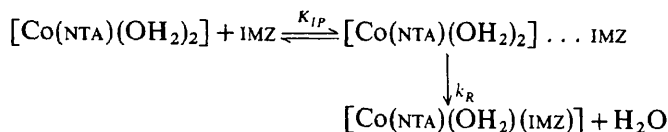


Figure 3. Plot of $k_{\text{obs}}(K_1 + [\text{H}^+])$ vs $[\text{H}^+]$ at 50°C , $[\text{complex}]_T = 5 \times 10^{-5} \text{ M}$, $[\text{IMZ}]_T = 1 \times 10^{-3} \text{ M}$, $\mu = 0.1 \text{ M}$, for the reaction of $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ with imidazole.

complex and imidazole respectively. As revealed from pH variation studies neutral imidazole species, denoted by $[\text{IMZ}] = K_a[\text{IMZ}]_T / (K_a + [\text{H}^+])$, takes part in the reaction. Hence under pseudo first-order conditions, the above equation reduces to

$$k_{\text{obs}} = \frac{a[\text{IMZ}]}{b + [\text{IMZ}]} \quad (11)$$

Two possible mechanisms which fit the above experimental rate law are I_d and D . For an I_d mechanism the following sequence of reactions may be envisioned to occur.

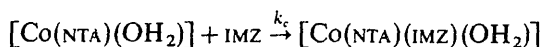
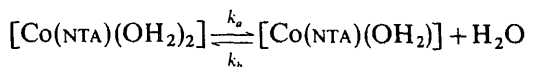


with

$$k_{\text{obs}} = \frac{k_R[\text{IMZ}]}{(1/K_{IP}) + [\text{IMZ}]} \quad (12)$$

The above parameters in (12) also take into account the contributions from the hydroxoquo species. The values of k_R correspond to a and those of $1/K_{IP}$ to b . Values of K_{IP} (ion pair formation constant) obtained from the plots of k_{obs}^{-1} vs $[\text{IMZ}]^{-1}$ are 44647, 18886 and 21550 at 40, 50 and 60°C respectively at pH 6-10. These values of K_{IP} are very large if one considers a 0, 0 or -1, 0 interaction. The large values of K_{IP} seem

If a *D* mechanism is operative, the following reaction sequence is applicable for the aquo species



th

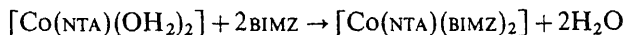
$$k_{\text{obs}} = \frac{k_a[\text{IMZ}]}{(k_b/k_c) + [\text{IMZ}]} \quad (13)$$

The k_a and k_b/k_c values have been extracted from the respective intercepts and slopes of the plots of k_{obs}^{-1} vs $[\text{IMZ}]^{-1}$ and are listed in table 1. The values of k_a correspond to *a* and those of k_b/k_c to *b*. It is to be mentioned here that these kinetic parameters should be treated as composite, since contribution from the hydroxo-aquo species is also present. From a temperature dependent study of k_a at pH 6-10, $\Delta H^\ddagger = 80 \pm 9 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -80 \pm 21 \text{ JK}^{-1} \text{ mol}^{-1}$ have been evaluated.

The conclusive piece of information supporting this *D* mechanism is obtainable from the invariance of k_a as the entering ligand is changed i.e., k_a should be independent of the entering ligand and would be unique to $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ in a particular solvent system. Till now no other ligand has been studied that reacts with $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ to give a rate law similar to (13). Hence we have attempted the reaction of *cis*- $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ with benzimidazole (vide supra). It is worthwhile to mention here that in the redox studies with this cobalt(III) species, Thacker and Higginson (1974) have noted that (i) the hydroxo-aquo species is more reactive than its conjugate acid, and (ii) the rate limiting step is a ligand substitution, involving replacement of the ligand entering by the reducing substrates. Finally the reactions have been designated as dissociative by observing the close similarity of rate constants for all the reductants studied.

Reaction of *cis*- $[\text{Co}(\text{NTA})(\text{OH}_2)_2]$ with benzimidazole

The rate studies have been carried out at ionic strength 0.1 M (NaClO_4) having $[\text{Co(III)}]_T = 5 \times 10^{-5} \text{ M}$ and $[\text{BIMZ}]_T = 2 \times 10^{-4} - 2 \times 10^{-3} \text{ M}$ at pH 5.60-6.85 and the results are summarized in table 2. The complexation occurs in one step with excellent retention of isosbestic points at 536, 444 and 390 nm for the entire course of the reaction. Absorbance changes are recorded with time at 580 nm where the change during the reaction is greatest. The stoichiometry of the reaction as studied by spectrophotometric titration (figure 2) is



The same arguments, as have been presented in imidazole substitution, can be drawn here to establish that the observed reaction is the entry of first benzimidazole. The plots of $\log(A_t - A_\infty)$ vs t are linear for more than three half-lives of the reaction. At pH 5.60 there is the possibility of the following two reactions occurring

Table 2. Kinetic data for the reaction of *cis*-[Co(NTA)(OH₂)₂] with benzimidazole.

Temperature (°C)	pH	[BIMZ] _T (× 10 ⁴ M)	<i>k</i> _{obs} (× 10 ⁵ sec ⁻¹)	<i>k</i> _a (× 10 ⁵ sec ⁻¹)	<i>k</i> _s / <i>k</i> _c (× 10 ⁴)
40	5.60	2	0.93	3.70	3.55
		3	1.31		
		4	1.60		
		5	1.71		
		6	1.95		
		8	2.11		
		10	2.18		
50	5.60	2	2.38	8.12	3.08
		3	3.17		
		4	3.63		
		5	4.12		
		6	4.67		
		8	5.12		
		10	5.31		
60	5.60	2	5.87	17.58	2.51
		3	7.98		
		4	9.37		
		5	10.21		
		6	11.52		
		8	12.67		
		10	12.86		
		20	13.24		
	5.85	10	17.08		
	6.10	10	25.33		
	6.50	10	28.02		
	6.85	10	32.63		

$\mu = 0.1 \text{ M (NaClO}_4\text{)}, [\text{complex}]_T = 5 \times 10^{-5} \text{ M.}$

But no usual substitution, rather a slow reduction from Co^{3+} to Co^{2+} is observed at $[\text{H}^+] > 1 \times 10^{-4} \text{ M}$. We have determined the acid dissociation constant (K_b) of benzimidazole by the pH-titration method (figure 4). The data give $pK_b = 5.47, 5.44, 5.39, 5.34$ and 5.29 at $25, 30, 40, 50$ and 60°C respectively at $\mu = 0.1 \text{ M (NaClO}_4\text{)}$. So this observation excludes the possibility of (15) occurring.

As shown in figure 5 the dependence of the pseudo first-order specific rate on $[\text{BIMZ}]$ shows rate saturation behaviour. Individual points shown in figure 5 have been determined experimentally, while the curve is calculated by substituting appropriate values of the rate constants into (13). The form of the curve implies that the rate-determining step involves rupture of the Co-OH_2 bond. By use of the mechanism represented in (16) and (17) and the steady-state approximation for the penta-coordinated species, $[\text{Co(NTA)(OH}_2\text{)}]$, k_{obs} for the anation process is described by (18).

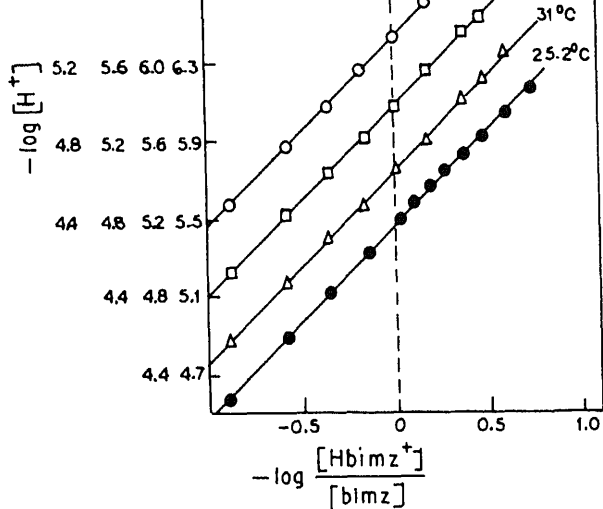


Figure 4. Graphical evaluation of the protonation constant (K_b) of benzimidazole at various temperatures. $[BIMZ]_T = 2 \times 10^{-3}$ M, $\mu = 0.1$ M ($NaClO_4$).

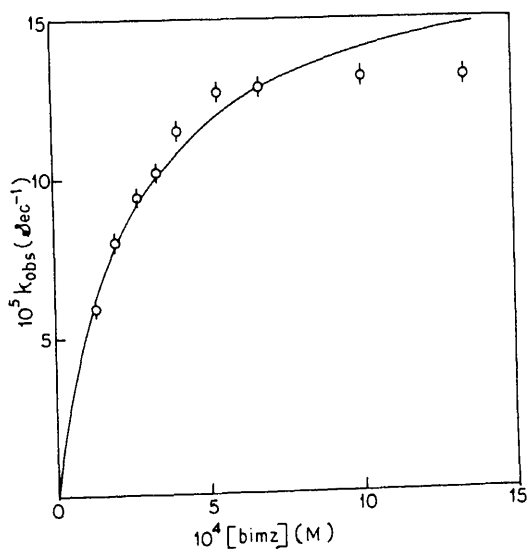
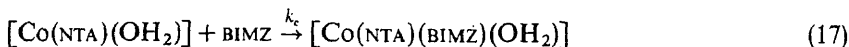


Figure 5. Plot of k_{obs} vs $[BIMZ]$ at 60°C, pH = 5.60, $\mu = 0.1$ M, $[complex]_T = 5 \times 10^{-4}$ M for the reaction of $[Co(NTA)(OH)_2]$ with benzimidazole.

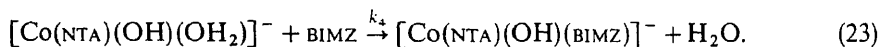
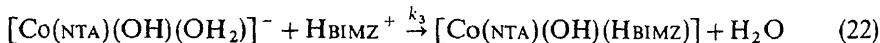
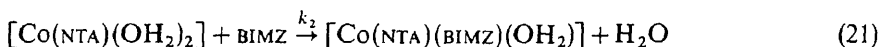


$$k_{\text{obs}} = \frac{k_a [\text{BIMZ}]}{(k_b/k_c) + [\text{BIMZ}]} \quad (18)$$

$$\frac{1}{k_{\text{obs}}} = \frac{k_b}{k_a k_c} \cdot \frac{1}{[\text{BIMZ}]} + \frac{1}{k_a} \quad (19)$$

At high $[\text{BIMZ}]$, $k_{\text{obs}} = k_a$ and the specific rate of the bond breaking step can be determined from the limiting rate in figure 5. At 60°C, pH = 5.60, $\mu = 0.1 \text{ M}$, this value is $(1.54 \pm 0.22) \times 10^{-4} \text{ sec}^{-1}$. The values of k_a and k_b/k_c obtained from the intercepts and slopes of the respective least-squares plots of k_{obs}^{-1} vs $[\text{BIMZ}]^{-1}$ are listed in table 2. The thermodynamic parameters obtained by using the k_a values at different temperatures are $\Delta H^\ddagger = 65 \pm 3 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -124 \pm 11 \text{ JK}^{-1} \text{ mol}^{-1}$.

pH variation studies have been performed at 60°C and at high benzimidazole concentration ($1 \times 10^{-3} \text{ M}$). The rate of the reaction increases slightly with the increase in pH. At higher pH values four reaction paths are possible:



The k_1 path has already been cancelled out by performing some experiments at pH < 4. The contribution of the k_3 path is also neglected by using treatment similar to that in the case of imidazole substitution. Invoking the remaining two paths, i.e., the reaction of diaquo and hydroxoquo complex with neutral benzimidazole, the rate law is

$$k_{\text{obs}} = \frac{k_2 [\text{H}^+] + k_4 K_1}{K_1 + [\text{H}^+]}$$

A unique plot of $k_{\text{obs}}(K_1 + [\text{H}^+])$ vs $[\text{H}^+]$ at $[\text{BIMZ}]_T = 1 \times 10^{-3} \text{ M}$ and at 60°C gives the value of k_2 and k_4 which indicate that the hydroxoquo complex is a little (≈ 1.25 times) more reactive than the diaquo form.

5. Conclusion

The specific rates for the formations of the monoimidazole and monobenzimidazole complexes are almost similar. The results are consistent with the view that the substitution processes are primarily dissociative, in which the loss of a coordinated water molecule from the inner coordination sphere of cobalt(III) is rate-determining. It

chromium(III). The water exchange rate (k_{ex}) of *cis*-[Co(NTA)(OH₂)₂] is not presently available. However it is not likely to be widely different from that of the *cis*-[Co(en)₂(OH₂)₂]³⁺ (en = ethylenediamine) having $k_{\text{ex}} = 7.7 \times 10^{-5} \text{ sec}^{-1}$ at 40°C (Krause and Taube 1961) or that of aquopentaamminecobalt(III) ion having $k_{\text{ex}} = 1 \times 10^{-4} \text{ sec}^{-1}$ at 45°C and at $\mu = 0.6 \text{ M}$ (Hunt and Taube 1958). A critical test of the dissociative mechanism lies in the fact that k_a should equal the rate constant for the water exchange reaction. The present results support this generalisation at least in a modest way. Tobe (1968) has argued that for a reaction proceeding through the *D* path, square-pyramidal intermediates are feasible. This would lead to a retention of configuration and negative $\Delta S^\ddagger$ values are expected. Moreover the $\Delta H^\ddagger$ values for the formation of both imidazole and benzimidazole complexes are highly positive while the corresponding $\Delta S^\ddagger$ values are highly negative. These parameters implicate a largely dissociative transition state in which the Co^{III}-OH₂ bond is strongly weakened.

Acknowledgement

Financial assistance received from CSIR, New Delhi, is gratefully acknowledged. Thanks are due to Dr M P Pujari for assistance.

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Ruthenium(III) catalyzed oxidation of 1-phenylethanol and substituted 1-phenylethanols by phenyliodosoacetate

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Abstract. Ruthenium(III) catalysed oxidation of 1-phenylethanol and substituted 1-phenylethanols by phenyliodosoacetate (PIA) in acetic acid is studied and a probable mechanism suggested. The proposed mechanism involves the formation of a complex of Ru(III) and (PIA) which reacts with the substrate, S, in a slow step. Spectrophotometric evidence for this complex is presented. Studies on the effect of substituents suggest a transition state involving a π -complex.

Keywords. Oxidation; 1-phenylethanol; Ru(III) catalyst; phenyliodosoacetate.

1. Introduction

Organic substrates like diols, cyclanols and unsaturated systems are oxidized by phenyliodosoacetate (PIA) in the presence of Ru(III) (Radhakrishnamurti and Panda 1979; Pati and Dev 1982). In the present work oxidation of 1-phenylethanol and substituted 1-phenylethanols has been investigated using Ru(III) chloride as the catalyst.

Oxidants like permanganate, chlorine and peroxydisulphate oxidize Ru(III) to higher oxidation states (Cotton and Wilkinson 1972). Of these, Ru^{6+} , Ru^{7+} and Ru^{8+} exist only in alkaline medium (Connick and Hurley 1952). A solution of RuCl_3 in acetic acid shows an absorption maximum at 460 nm (figure 1a). A mixture of RuCl_3 and excess of PIA shows an absorption maximum at 385 nm (figure 1b). PIA absorbs below 320 nm (figure 1c). The spectral pattern does not change on adding 1-phenylethanol to RuCl_3 in acetic acid (figure 1a). On adding the substrate to the reaction mixture containing RuCl_3 and PIA, the spectral pattern is similar to that of RuCl_3 . This suggests that the catalyst is released from the complex during the course of the reaction. EPR studies reveal the same splitting pattern for both RuCl_3 and for the mixture of RuCl_3 and PIA, indicating that there is no change in the oxidation state of Ru(III).

2. Experimental

1-Phenylethanol (Fluka) and ruthenium(III) chloride [Johnson Matthey (London)] were used as such. Acetic acid (BDH, AR) was purified by the method due to Orton (Orton and Bradfield 1950), potassium permanganate being used instead of chromic acid. The fraction boiling between 117° and 118°C (freezing point = 16.4°C) has been

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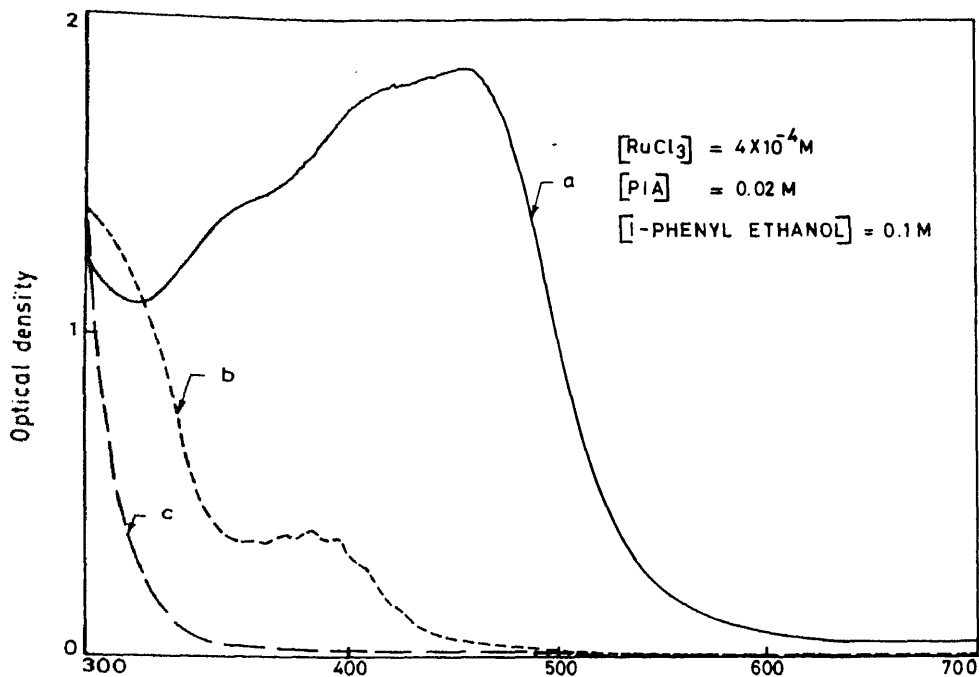


Figure 1. Absorption spectra of **a.** $RuCl_3$ in acetic acid and a mixture of $RuCl_3$ and 1-phenylethanol, **b.** a mixture of $RuCl_3$ and excess of PIA, and **c.** PIA alone in acetic acid.

used. Phenyliodosoacetate (melting point = $158^\circ C$) was prepared by the modified method of Boeseken (Boeseken and Schneider 1931). Solutions of ruthenium(III) chloride in acetic acid were standardised by the method of Horiuchi (Horiuchi and Ichiyyo 1970). All the reactions have been carried out in glacial acetic acid at $35 \pm 0.1^\circ C$. The progress of the reaction was monitored by determining the concentration of unreacted PIA, iodometrically, at any instant as a function of time.

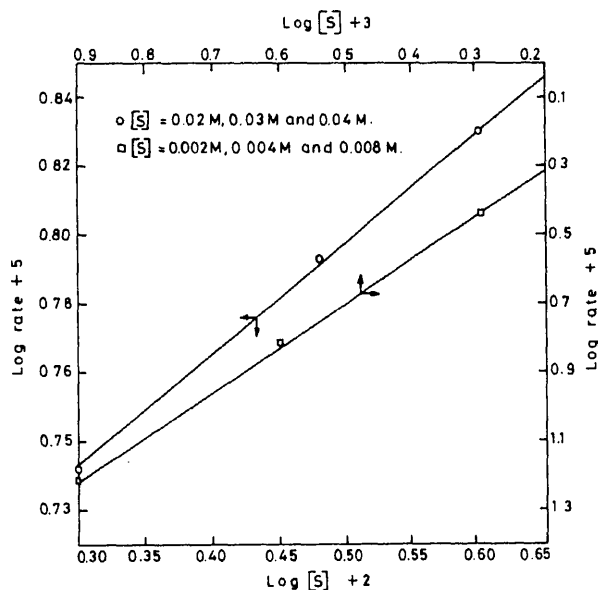
3. Results and discussion

The product of the reaction is found to be acetophenone by TLC, GLC and from the melting point of the 2,4-dinitrophenylhydrazone ($250^\circ C$). The reaction follows 1:1 stoichiometry under all conditions, i.e. whether PIA or alcohol is in excess. The amount of ketone formed corresponds to that of PIA consumed. The concentration of the ketone has been determined spectrophotometrically by measuring the absorbance at 500 nm of a wine-coloured quinonoid compound (Lappin and Clark 1951) obtained by the action of KOH on a solution of the 2,4-dinitrophenylhydrazone in alcohol. The phenylhydrazine is not affected by the alkali and it absorbs only at 255 nm and 350 nm. The reaction is found to be first order in PIA and first order in catalyst (table 1). The

Table 1. Effect of varying the concentrations of PIA, Ru(III) and substrate on the rate of the reaction.

[PIA] (M)	[S] (M)	[Ru(III)] $\times 10^6$	$k' \times 10^3$ (min^{-1})	$k_1 \times 10^{-3}$ ($\text{M}^{-1} \text{min}^{-1}$)
0.006	0.10	2.0	4.88	2.55 ± 0.10
0.005	0.10	2.0	5.32	
0.004	0.10	2.0	5.28	
0.003	0.10	2.0	4.90	
0.010	0.10	2.0	5.30	2.59 ± 0.06
0.010	0.10	3.0	7.53	
0.010	0.10	4.0	10.40	
0.010	0.15	2.0	5.29	2.55 ± 0.07
0.010	0.25	2.0	5.06	
0.010	0.35	2.0	4.95	

Solvent: glacial acetic acid; temperature: 35°C; k' = pseudo first order rate constant; k_1 = second order rate constant.

**Figure 2.** Plots of log rate versus log $[S]$ for low concentrations of the substrate.

ixture. An equilibrium step involving the formation of acetophenone is therefore

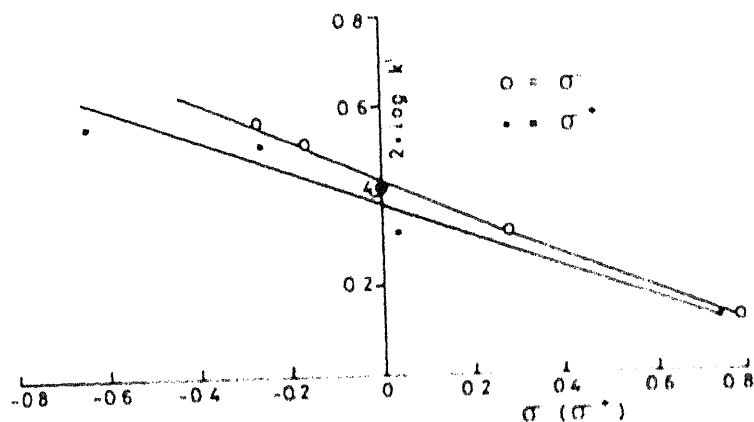


Figure 3. Variation of $\log k$ versus σ (σ^+)

Table 2. Pseudo-first order rate constants for the oxidation of a few *p*-substituted 1-phenylethanols and their corresponding substituent constants [Substrate] = 0.1 M, [Pb] = 0.01 M, [catalyst] = 1.0×10^{-3} M, solvent = 100% acetic acid temperature = 35°C

Substituted 1-phenylethanol	$2 + \log k$	σ^+	σ
1-(4-Nitrophenyl)ethanol	0.120	0.34	0.78
1-(4-Chlorophenyl)ethanol	0.320	0.04	0.28
1-Phenylethanol	0.415	0	0
1-(4-Methylphenyl)ethanol	0.519	0.26	0.17
1-(4-Methoxyphenyl)ethanol	0.571	0.65	0.24

σ^+ values from Swain C G and Lupton F C 1968 *J. Am. Chem. Soc.* **90** 4128
 σ values from Hammett L P 1940 *Physical organic chemistry*, 2nd ed. (New York: McGraw-Hill) p. 356

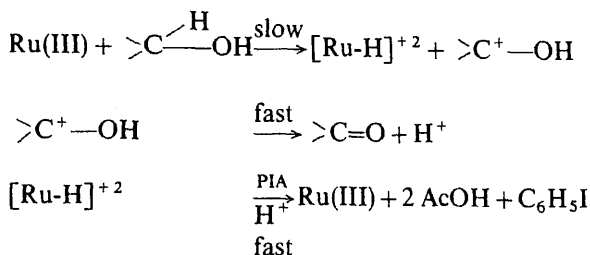
determining step. However due to the small value of ρ it cannot be used unequivocally for mechanistic discrimination.

3.1 Mechanism and rate law

The absence of polymerization of acrylamide added to the reaction mixture indicates that the reaction is not proceeding by a free radical pathway. For Ru(III) catalyzed oxidation, three types of mechanisms could be proposed.

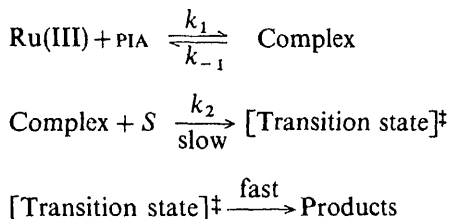
(scheme 2) proposed by Singh (Singh *et al* 1977) to explain the first order in the substrate and zero order in PIA is not applicable for the reaction under consideration since the order with respect to PIA is found to be unity. Moreover IR studies do not show any stretching frequency due to Ru-H at 2020 cm^{-1} (Hallman *et al* 1968).

Scheme 2



Scheme 3 accounts for all the experimental observations satisfactorily.

Scheme 3



The rate expression for the above scheme is given as,

$$\text{Rate} = \frac{k_1 k_2 [\text{S}] [\text{Ru(III)}] [\text{PIA}]}{k_{-1} + k_2 [\text{S}]} \quad (1)$$

Equation (1) can be rearranged to give (2).

$$\frac{1}{\text{Rate}} = \frac{k_{-1}}{k_1 k_2 [\text{S}] [\text{Ru(III)}] [\text{PIA}]} + \frac{1}{k_1 [\text{Ru(III)}] [\text{PIA}]} \quad (2)$$

A plot of $1/\text{rate}$ versus $1/[\text{S}]$ for low concentrations (0.02 to 0.08 M) of the substrate at constant concentrations of Ru(III) and PIA is linear (figure 4). From the intercept k_{-1} found to be 2.9×10^3 . From the slope and the intercept the value of $k_{-1}/k_2 = 0.01$. This value is sufficiently small to justify the assumption that $k_{-1}/k_2 \ll [\text{S}]$ for high concentrations of the substrate (0.1 to 0.35 M) where the order in substrate is found to be zero. Under these conditions the rate expression (1) reduces to

$$\text{Rate} = k_1 [\text{Ru(III)}] [\text{PIA}].$$

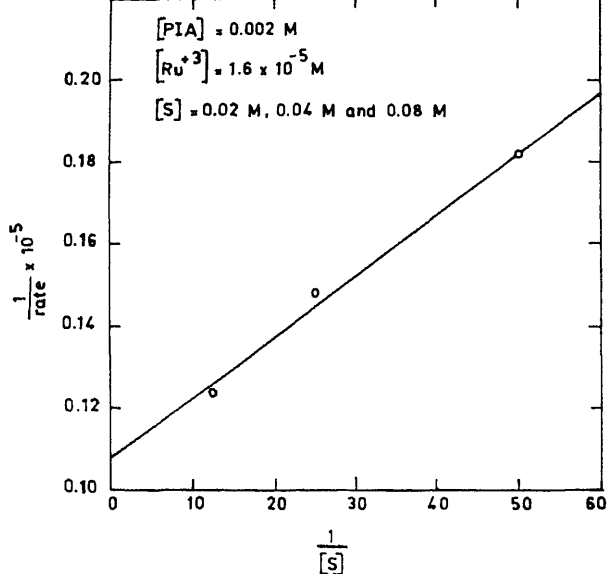


Figure 4. A plot of $1/\text{rate}$ versus $1/[S]$.

above accounts for all the experimental observations in Ru(III)-catalyzed oxidation of 1-phenylethanol.

Acknowledgements

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Magnetic, spectral and thermal properties of some new coordination polymers

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Abstract. A tetradentate poly Schiff base ligand has been prepared from 4,4'-dihydroxy-3,3'-diacetyl biphenyl with *o*-dianisidine. Polychelates of this ligand have been prepared from metal acetates of the first transition series. The stereochemistry of these polychelates has been discussed in terms of their magnetic behaviour, IR and diffuse reflectance spectra, and thermal and elemental analyses. All the polychelates are dark in colour and are insoluble in common organic solvents.

Keywords. 4,4'-Dihydroxy-3,3'-diacetyl biphenyl; *o*-dianisidine; polychelates; DMF.

1. Introduction

The importance of coordination polymers of Schiff-base ligands in inorganic chemistry is seen by the large number of publications (Horowitz *et al* 1965; Chakravarty and Drinkard 1960). Some of the polymers containing metal ions linked by chelate rings from organic groups show exceptional thermal stability.

We intend in this present survey to reconsider some of the properties of a restricted number of the polychelates, especially their stereochemistry and thermal stability. An attempt has been made to characterize these compounds by elemental analysis, magnetic behaviour, diffuse reflectance spectra, IR spectra and thermal analysis.

2. Experimental

2.1 Preparation of ligand

The hydroxy ketone 4,4'-dihydroxy-3,3'-diacetyl biphenyl (DABP), and the aromatic diamine *o*-dianisidine (DA), were dissolved separately in hot ethanol in a 1:2 stoichiometric ratio and mixed. The reaction mixture was refluxed for 10 hr. On cooling, dark yellow coloured psb (poly schiff base) separated out, which was filtered, washed with ethanol and dried. It was insoluble in common organic solvents but was soluble in DMF, DMSO and H₂SO₄. The polymeric Schiff base so prepared may act as a quadridentate ligand.

2.2 Preparation of the polychelates

The polychelates of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) were prepared by

and mixing. The reaction mixture was refluxed for 6 hr. The hot solution was poured into crushed ice. The precipitates were allowed to settle down, then were filtered, washed with hot water and dried. The polychelates were insoluble in common organic solvents and were purified by soxhlet extraction in methanol to remove impurities and dried.

2.3 Elemental analyses

Carbon, hydrogen and nitrogen were analysed by a Coleman C-H-N analyzer.

2.4 Metal content in the complexes

The metal content was determined by the EDTA titration technique after decomposition of the polychelates.

2.5 Physical measurements

The magnetic susceptibility of the polychelates was determined by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. IR spectra were scanned in KBr on a Carl Zeiss Jena UR-10 spectrophotometer. Electronic spectra were obtained from a Beckman DU spectrophotometer using MgO as reference. Thermogravimetric (TG) analysis was carried out on a 'Linseis thermogravimetric analyzer' in air at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

In a system like this it is likely that extensive cross linking of the macromolecules exists, which makes polychelates insoluble. Due to insolubility of the polychelates in common organic solvents, it was not possible to characterize them by conventional techniques, such as viscosity, osmometry, etc. The analytical data are summarized in table 1 and support the formulae assigned to them.

Table 1. Analytical and magnetic moment data.

Compound	Colour		Elemental analysis				μ_{eff} (BM)
			M%	C%	H%	N%	
DABP DA	Dark yellow	Calc.	—	70.00	5.83	5.44	—
		Found		70.85	5.40	6.00	
$\text{Cu}[\text{DABP DA}]$	Brick red	Calc.	11.03	62.57	4.86	4.86	1.87
		Found	10.75	62.10	4.55	5.12	
$\text{Ni}[\text{DABP DA} \cdot 2\text{H}_2\text{O}]$	Brown	Calc.	9.67	59.36	5.27	4.61	2.82
		Found	9.25	59.72	5.42	4.22	
$\text{Co}[\text{DABP DA}]$	Brown	Calc.	10.31	63.08	4.90	4.90	4.10
		Found	10.72	63.62	4.40	4.61	
$\text{Mn}[\text{DABP DA} \cdot 2\text{H}_2\text{O}]$	Dark brown	Calc.	9.10	59.73	5.30	4.64	5.90
		Found	8.88	59.20	5.65	4.00	
$\text{Zn}[\text{DABP DA}]$	Brick red	Calc.	11.01	62.59	4.86	4.86	Diamagnetic
		Found	11.25	62.10	4.42	4.12	

Cu(II) polychelate shows a magnetic moment 1.87 BM which is slightly higher than the spin only value of a one unpaired electron (1.73 BM) for a square planar environment (Mahapatra and Rama Rao 1972). The excess of the magnetic moment over the spin only value may be due to orbital contribution (Baker *et al* 1966). The magnetic moment of Ni(II) polychelate is 2.82 BM which is in the range expected for the spin only value for two unpaired electrons in an octahedral or distorted octahedral geometry (Nyholm 1953). Cobalt (II) polychelate exhibits a magnetic moment of 4.10 BM. The low value could be indicative of the presence of a mixture of high spin tetrahedral and low spin planar forms (Calvin and Barkelew 1946). The room temperature magnetic moment of manganese(II) polychelate is 5.90 BM which conforms well with the spin only moment for an octahedral stereochemistry (Siddiqi *et al* 1982). Zinc (II) polychelate is diamagnetic as it has no unpaired electron.

The electronic spectrum of copper (II) complex shows three bands at 24 390, 18 350 and 14 600 cm^{-1} . The band at 24 390 cm^{-1} may be assigned to charge transfer or intraligand transition (Sacconi and Ciampolini 1964). The other two bands are *d-d* transitions for which a planar structure is proposed (Patel and Patil 1981). Nickel (II) polychelate exhibits bands at 22 000, 16 130, 9050 and 8660 cm^{-1} . The position of these transitions is consistent with those of an octahedral, essentially distorted structure (Rastogi and Sharma 1974). The γ_1 transition is found to split into two bands (9050 and 8660 cm^{-1}) which can be assigned to the transition arising from the splitting of the $^3T_{2g}(F)$. The Racah parameter, B_{35} , is calculated using the method suggested by Konig (1971). Transition energies γ_2 and γ_3 are calculated using the Racah parameter (table 2). In nickel (II) polychelate having octahedral geometry, the value of γ_1 corresponds to 10 D_q which is calculated using the Konig (1971) equation (table 2). An attempt has been made to compute the repulsion parameter using the splitting values γ_1 and γ_2 by known methods (Rastogi and Sharma 1971; Lever 1968).

Table 2. Spectral data of the polychelates.

Compound	Energies (cm^{-1})		Assignment
	Observed	Calculated	
Cu[DAMP DA]	14 600	—	$^2B_{1g} \rightarrow ^2A_{1g}$
	18 350	—	$\rightarrow ^2E_g$
	24 390	—	charge transfer
Ni[DABP DA · 2H ₂ O]	8660	8660	$^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$
	9050	—	—
	16 130	14 160	$\rightarrow ^3T_{1g}(F)$
	22 000	23 970	$\rightarrow ^3T_{1g}(P)$
Co[DABP DA]	—	4115	$^4A_2 \rightarrow ^4T_2(F)$
	8930	9665	$\rightarrow ^4T_1(F)$
	16 100	15 335	$\rightarrow ^4T_1(P)$
	25 000	—	charge transfer
Mn[DABP DA · 2H ₂ O]	15 270	—	$^6A_1(S) \rightarrow ^4T_{1g}(G)$
	18 690	—	$\rightarrow ^4T_{2g}(G)$

$$D_{35} = 810 \text{ cm}^{-1}, \quad p_{35} = 0.75, \quad D_1 = 44.57 \text{ cm}^{-1}, \\ D_q = 866.00 \text{ cm}^{-1}, \quad D_{q(av)} = 827.00 \text{ cm}^{-1},$$

$$\gamma_2/\gamma_1 = 1.86 \text{ and LFSE (ligand field splitting energy) = } 29.70 \text{ kcal/mol.}$$

The reflectance spectrum of cobalt (II) complex under study shows bands at 16 100 and 8930 cm^{-1} which may be assigned to tetrahedral geometry (Patel and Patil 1982). The band at 25 000 cm^{-1} may arise due to charge transfer or internal ligand transitions (Sacconi *et al* 1962). The transition energies $\gamma_1, \gamma_2, \gamma_3$ have been calculated using the equation applied for nickel (II) polychelate (table 2). The value of B_{35} is calculated by the Konig (1971) relation. The calculated values of B_{35}, β_{35} and LFSE are found to be 877.9 cm^{-1} , 0.78 and 14.39 kcal/mol respectively. The electronic spectrum of manganese (II) polychelate exhibits three weak bands at the expected positions for an octahedral environment (Bates *et al* 1966). The zinc (II) complex is diamagnetic and may have tetrahedral geometry.

The IR spectra are complicated and difficult to interpret. However, only those peaks that could be assigned with reasonable certainty are listed. The spectra indicate strong C=N stretch in the ligand at 1620 cm^{-1} which shows either a positive shift (Busch and Bailar 1956) or a negative shift (Lal *et al* 1978) on complexation. However, in some cases there is no shift at all (Sharma and Bailar 1955). In Co(II), Mn(II) and Zn(II) polychelates the C=N stretch is shifted to higher frequency while in the case of Ni(II) polychelate it is slightly shifted to lower frequency. In Cu(II) polychelate it is not shifted at all. The medium band observed at 1280 cm^{-1} which may be phenolic C-N stretch vibration in the ligand shifted to a higher wavenumber, indicating that oxygen is involved in bonding (Biradar and Kulkarni 1971). Ni(II) and Mn(II) polychelates exhibit bands in the region 790–830 cm^{-1} and 1590–1600 cm^{-1} . These bands are attributed to coordinated water (Nakamoto 1963) and confirmed from TG analysis.

Thermal decomposition data are summarized in table 3. Goodwin and Bailar (1961) observed the given thermal stability order for the polychelates as Ni > Cu > Co which is in agreement with the observation reported by Marvel and Tarkoy (1958). We have observed the change in thermal stability order at 300°C as Co > Ni > Mn > Cu. The magnitude of water molecule was calculated by taking the residue of decomposition at ~ 200°C. The thermal activation energy was calculated by employing the Broido (1969) method.

Table 3. Thermal data of the polychelates.

Compound	Decomposition Temperature (°C)	% Weight loss at temperature						Ea (kcal/mol)
		100	200	300	400	500	600	
DABP DA	250–335 425–510	0.0	1.0	27.00	43.5	83.00	90.00	30.66, 19.1
Cu[DABP DA]	235	0.0	0.5	42.00	82.5	87.5	91.00	29.05
Ni[DABP DA · 2H ₂ O]	270	0.0	6.00	20.5	77.0	88.0	91.00	19.55
Co[DABP DA]	245	0.0	0.00	14.5	69.0	80.0	84.00	27.14

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Erratum

'Thermal decomposition of some nitroanilinoacetic acids' by K U B Rao and S R Yoganarasimhan, Proc. Indian Acad. Sci. (Chem. Sci.), 95, pp. 309-314, 1985.

Line 6 in table 2 should be read as

179 5.91 224 8.92 $M^+ - \text{COOCH}_2\text{CH}_3 - \text{OH}$

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